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FINAL REPORT

Project No. A-360

STUDY OF AGING EFFECTS OF QUARTZ CRYSTAL PLATES

by

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Contract No. DA-36-039-SC-74946
Department of the Army Project: 3-99-12-102

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1 August 1957 to 31 July 1958

The object of this investigation is to study the effects of presently used frequency adjustment techniques on the stabilities of plated quartz resonators

Placed by the U. S. Army
Signal Engineering Laboratories
Fort Monmouth, New Jersey

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SECTION I

PURPOSE

The purpose of Contract No. DA-36-039-SC-74946 is to determine the effect of frequency adjustment, by overplating or deplating techniques, on the stability of plated AT-cut quartz resonators, and to establish procedures that may be expected to give units of consistently superior stability. A second but subsidiary purpose is to continue studies of the agencies contributing to the aging of quartz resonators as outlined in previous Contracts Nos. DA-36-039-SC-147, DA-36-039-SC-42453, DA-36-039-SC-56753, and DA-36-039-SC-64613.

II. ABSTRACT

In order to determine the effect of the frequency adjustment step on the stabilities of 16.5 mc AT-Cut quartz resonators, 250 resonators have been fabricated and tested. The frequencies of these have been measured at constant temperature of 85°C over periods of 60 to 180 days. Among the resonators fabricated were 58 plated with a single coat of evaporated gold and mounted in the HC-6/U cans or in glass containers by methods known to give high stability, 76 similarly mounted but overcoated to frequency subsequently with a second coat of evaporated or electroplated gold, and 20 frequency adjusted by partially deplating the single layer plating by positive ion bombardment or by using the Tesla discharge technique. The use of reclaimed resonator blanks and containers for the first 79 units fabricated contributed to a greater variation in data than was expected. However, data obtained subsequently with new blanks and containers verified, in general, the results obtained from earlier data. Overplating a gold plated resonator with a second coat of gold for frequency adjustment did not appreciably degrade the frequency stability of the original resonator whether the overplate was applied by evaporation or electroplating. In contrast to this, electroplated nickel applied to goldplated units as the overcoat resulted in marked upward drifts of the resonator; this was ascribed to residual stress in the electroplated film. In the limited number of tests conducted, adjustment by ion bombardment for a range of several thousand cycles did degrade the frequency stabilities of the original units. Of 65 resonators plated by evaporation of a single coat of aluminum on the hot (450°C or 200°C) quartz substrate 32 exhibited frequency drops of 0.0002 to 0.0006 percent in 60 days and thereafter stabilized at slopes of less than 0.00005 percent per month. The bulk of those in metal containers that did not stabilize proved to be leakers. Aluminum plated resonators sealed in glass were not markedly better than those mounted in metal containers. Increases in the R_s of a few resonators, apparently as a result of oxidation of the thin aluminum film, impressed an upward drift on a few resonators. The latter cancelled a part of the normal downward drift resulting in overall higher stability for units displaying this effect.

Ten resonators plated by evaporation of a single coat of silver on the hot (200°C) quartz substrate mounted in the HC-6/U container exhibited stabilities nearly equivalent to the gold plated resonators.

Unexpected downward drifts of a large number of gold plated resonators led to the examination of all units for leaks by a vacuum leak test conducted with the units immersed in Octoil. Cracks of the glass type bases of the HC-6/U containers were found in a high percentage of units. These developed upon the act of inserting the resonators in tight sockets of the constant temperature oven and vitiated much of the collected stability data. Different rates of drift appeared to be proportional to different sizes of microleaks. Leaks in the HC-6/U containers produced in this and other innocuous appearing manners seem to be responsible for much of the loss of stability of units mounted in that container. The value of the glass containers for both experimental studies and practical use is that it is not subject to the development of micropores with time; the development of these appears to be an intrinsic weakness of the HC-6/U containers as now designed and sealed.

SECTION III

PUBLICATIONS, LECTURES, REPORTS AND CONFERENCES

Visits to the Signal Engineering Laboratories were made by members of the research team of the Georgia Institute of Technology on 1 October 1957, 5-8 May 1958 and 10 July 1958 for discussions on the progress and programming of the work with the Project Engineer, Mr. P. E. Mulvihill, and other members of the staff of the Signal Engineering Laboratories.

On 6 May 1958 Mr. R. B. Belser presented a review of the progress on the project at the 12th Annual Frequency Control Symposium held at Asbury Park, New Jersey.

Visits to other organizations included one by Mr. Belser on 3 November 1958 to Union Thermoelectric Corporation, Forest Park, Illinois for discussions with Mr. R. D. Cortright concerning procurement of polished AT-cut quartz crystal blanks, and one to Wright Air Development Center by Mr. Belser and Mr. W. H. Hicklin to present papers on studies of "The Electrical Conductivities of Metallic Films in the Temperature Range 25°C to 600°C." The latter was presented at the Symposium on Metal Film Resistor Processes, Techniques and Capabilities at Wright Air Development Center, Wright-Patterson Air Force Base, Ohio on 20 November 1957. The latter paper is to be published in the Proceedings of the Symposium. Most of the information is included in Wright Air Development Technical Report 57-660, Astia Document 155 573, distributed in July 1958.

Papers covering the "Temperature Coefficients of Resistance of Metallic Films in the Range 25°C to 600°C" and "The Alloying of Bimetal Films, Simultantously or Successively Deposited" have been forwarded by Mr. Belser and Mr. Hicklin to the Journal of Applied Physics for publication.

IV. FACTUAL DATA

A. INTRODUCTION

In the Proceedings of the 11th Annual Symposium on Frequency Control[1] and in the Final Report[2] of Contract No. DA-36-039-SC-64613 methods for the plating and mounting of AT-Cut quartz resonators of high stability were outlined. Of 200 units fabricated and tested over 80 percent exhibited drifts of less than 0.00005 percent per month during six-month test periods, and many exhibited no directional drift within the accuracy of the measurements, one part in 10^7. This stability was maintained by gold plated units, coated by evaporation of gold onto hot quartz ($450^\circ C$), without regard to the type of container, whether glass, the HC-6/U can of nickel-silver or of nearly pure copper. Although a higher incidence of instability occurred in the metal containers this fact was related to the higher incidence of leaks occurring both initially and subsequently during the life of the unit. It was concluded, therefore, that quartz resonators fabricated in the manner described, with meticulous care, should be stable within the frequency range stated.

Since the coating method used incorporated only the base coating step, without a subsequent step for overcoating or adjusting to frequency, it appeared desirable to delineate the degradation of frequency occurring as a result of the latter step and to determine the method of frequency adjustment of minimum frequency degradation.

This phase of the work was undertaken during the past year.

B. APPARATUS AND PROCEDURES

The apparatus and procedures for base coating and frequency measurement were outlined in detail in the references[1,2] cited. The apparatus and procedures used for this phase have been outlined in detail in Quarterly Reports[3] 1-3 of this contract, No. DA-36-039-SC-74946. In the interest of brevity these matters will be reviewed here to the minimum extent compatible with clarity.

1. Quartz Blanks

In the initial phases of the work no resonator blanks were available other than those already coated and mounted during the previous contract. Approximately 79 units were salvaged and used in subsequent experiments. In general only units mounted in metal cans were salvageable; removal of the can was accomplished with a jig assembly which maintained alignment between the can and the crystal during this act.

Salvaged resonators were reprocessed for further study as outlined below.

30 were overcoated directly with evaporated gold and recanned in the same HC-6/U containers

10 were deplated by positive ion bombardment and recanned in the same HC-6/U containers

10 were deplated by Tesla-discharge coil and recanned in the same containers

5 were dismounted, overcoated and recanned in a glass container

20 were dismounted, chemically cleaned of plating and recoated with a base coat only of evaporated aluminum

Meticulous and careful dismantling procedures were used throughout. In spite of this fact, an element of doubt remained as to the quality of the blanks used in the early phase and the influence of the quality of the blanks on the reported data.

Subsequently 150 blanks were obtained from a commercial source and used in the additional work. Cleaning and mounting procedures described in the cited references were used.

2. Base Plating

Polished or semi-polished AT-cut quartz plated of high quality and of approximately 16.5 mc fundamental frequency were subjected to careful cleaning as outlined below. The blanks were successively:

a. immersed in agitated hot chromic acid;

b. rinsed thoroughly with hot distilled water;

c. loaded in batches of 20 into a teflon jig and immersed for periods of 3.0 to 4.5 minutes in a saturated solution of ammonium bifluoride maintained at room temperature;

d. immersed in a strong alconox solution;

e. rinsed in hot distilled water;

f. dried; and

g. stored in a desiccator or a petri dish placed in an oven held at 60°C.

As the storage time of step g was of an indefinite duration up to several weeks the blanks, before plating, were subjected to the recleaning process of steps a and b, drying with clean lens tissue, and final cleaning by the discharge from a hand held Tesla discharge coil. They were then loaded into a clean aluminum mask, placed in the vacuum chamber and plated with the selected metal. Delays between final cleaning and plating were held to the minimum practicable.

The aluminum mask for holding crystal blanks was cleaned by ion bombardment in the vacuum chamber, 10 minutes at 50 ma and 2500 volts, prior to loading it with the cleaned quartz blanks. The mask and included blanks were suspended from the top of a 4-inch pipe cross and the chamber was evacuated. The quartz blanks were heated to 450°C, as registered by a thermocouple near the mask, by radiant heat from auxiliary filaments located in both horizontal arms of the cross. This temperature was maintained for approximately ten minutes. At the close of this period gold coats of about 1500 Ångstroms thickness were evaporated onto each face of the quartz blanks simultaneously from filaments positioned near the heater filaments.

The blanks were subsequently mounted in the HC-6/U containers or in glass containers with careful attention to each detail of storage or fabrication. DuPont No. 5605 or Hanovia No. 2 silver cements were used to bond the coated quartz plate to the supporting spring clip or wire and to establish contact to the gold electrode.

3. Overcoating by Evaporation

Overcoating was normally done after storage of the resonator for a period of 24 or more hours in a covered petri dish. The units were carefully recleaned by rinsing in methanol of high purity. Overcoating was accomplished by evaporation of gold onto both sides of the blank simultaneously. A mask was used to position the gold spots centrally on each unit over a diameter of about 5/32-inch. In Figure 1 may be seen a typical overcoating setup. The frequency was measured in argon at atmospheric pressure before and after plating. In addition to the regular measuring equipment, a frequency meter, BC 221, was used during overplating to obtain an aural aid adjustment. The meter was preset to the desired frequency and the gold was evaporated until a zero beat was obtained.

In general the plating, overcoating and mounting of new and old blanks were accomplished in a similar manner. In a few instances the blanks were plated and not removed from the mask before overcoating, although they were exposed to air prior to the latter step. Frequency adjustments by evaporation were generally in the range 2000 to 12,000 cycles per second.

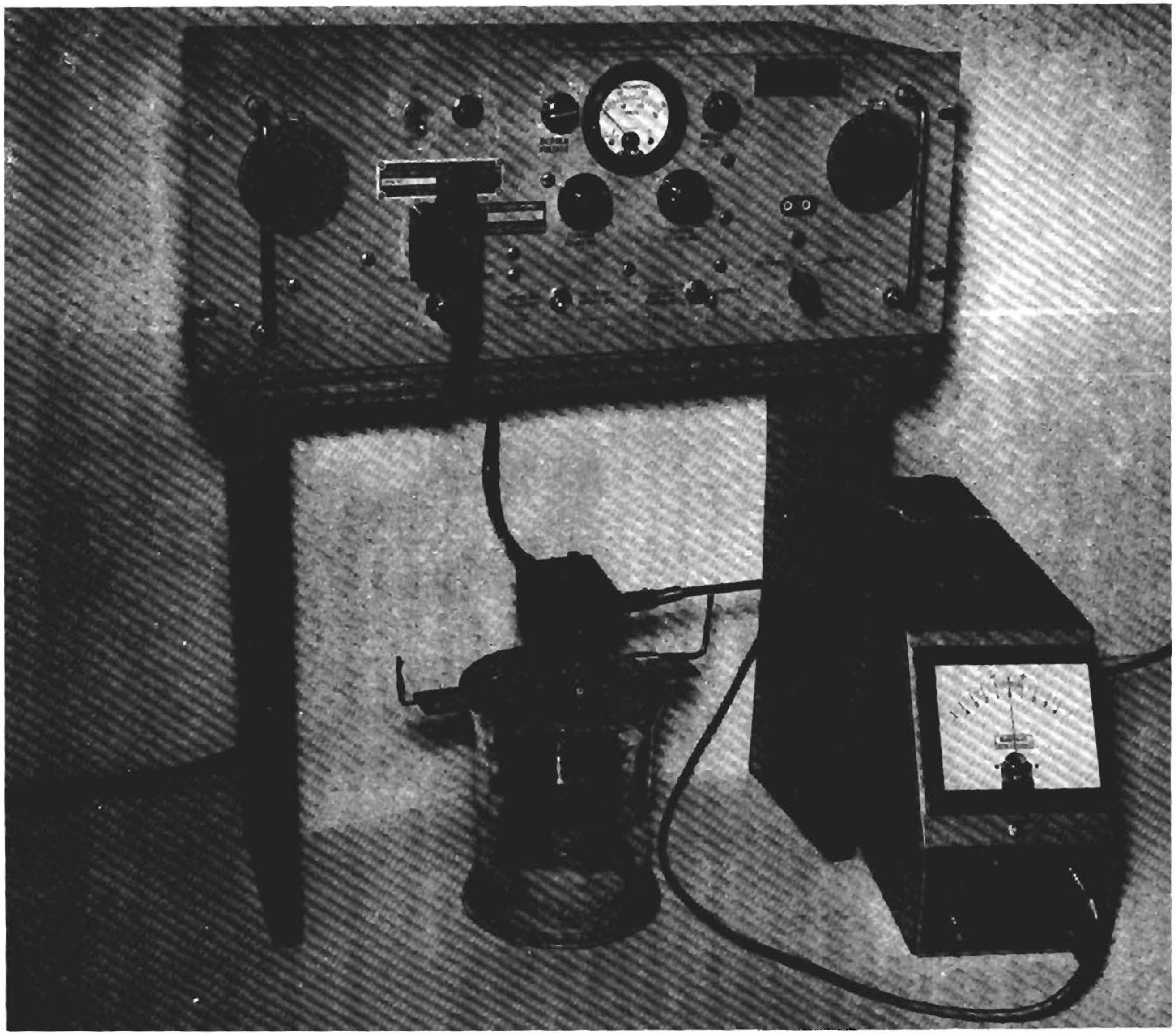

Figure 1. Vacuum Chamber and Monitoring Apparatus for Overcoating to Frequency.

4. Overcoating by Electroplating

In the last quarter a number of units were overcoated to frequency by electroplating over a base plate of gold deposited as described above.

The base plated blanks were first mounted and bonded; they were then thoroughly cleaned by gently scrubbing the resonators with a pipe cleaner and an alconox solution. This action was followed by several rinses in distilled water. The units were then separately made the cathode in a small beaker of electroplating solution and immersed for periods of 5 to 30 seconds at approximately 4 ma of current. Plate backs of -600 to -186,000 cycles were performed.

Units were plated with electroplated gold using a solution made from Sel-Rex Bright Gold B-1 Salts furnished by Precision Metals, Inc., Belleville, New Jersey.

Resonator blanks were plated with nickel using a solution obtained from a commercial plating firm.*

Some units after base plating appeared to be coated with deposits of vacuum oil condensed from the oil pump vapors. These did not electroplate well even after severe scrubbing. The gold base plate however withstood the cleaning treatment described above with no apparent ill effects.

5. Deplating

Deplating was accomplished by ion bombardment of the plated blanks positioned between two electrodes and by the Tesla discharge technique. A proper mask was not constructed in the studies reported and further studies of this technique will be required for proper evaluation of the technique.

Deplating by the hand held Tesla Discharge Coil proved difficult to control and severely increased the R_s values of the units treated. These increases were so large that stability measurements of these units were not made.

6. Aluminum Plated Resonators

Resonator blanks cleaned and heated *in vacuo* as for gold were coated with evaporated aluminum plating. These were not overcoated before stability

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*Approximate composition stated for Nickel Bright plating solution is:

Single nickel salts	$NiSO_4$	30 to 50 oz. per gal.
	$NiCl_2$	4 to 8 oz. per gal.
	H_3BO_4	4 to 6 oz. per gal.

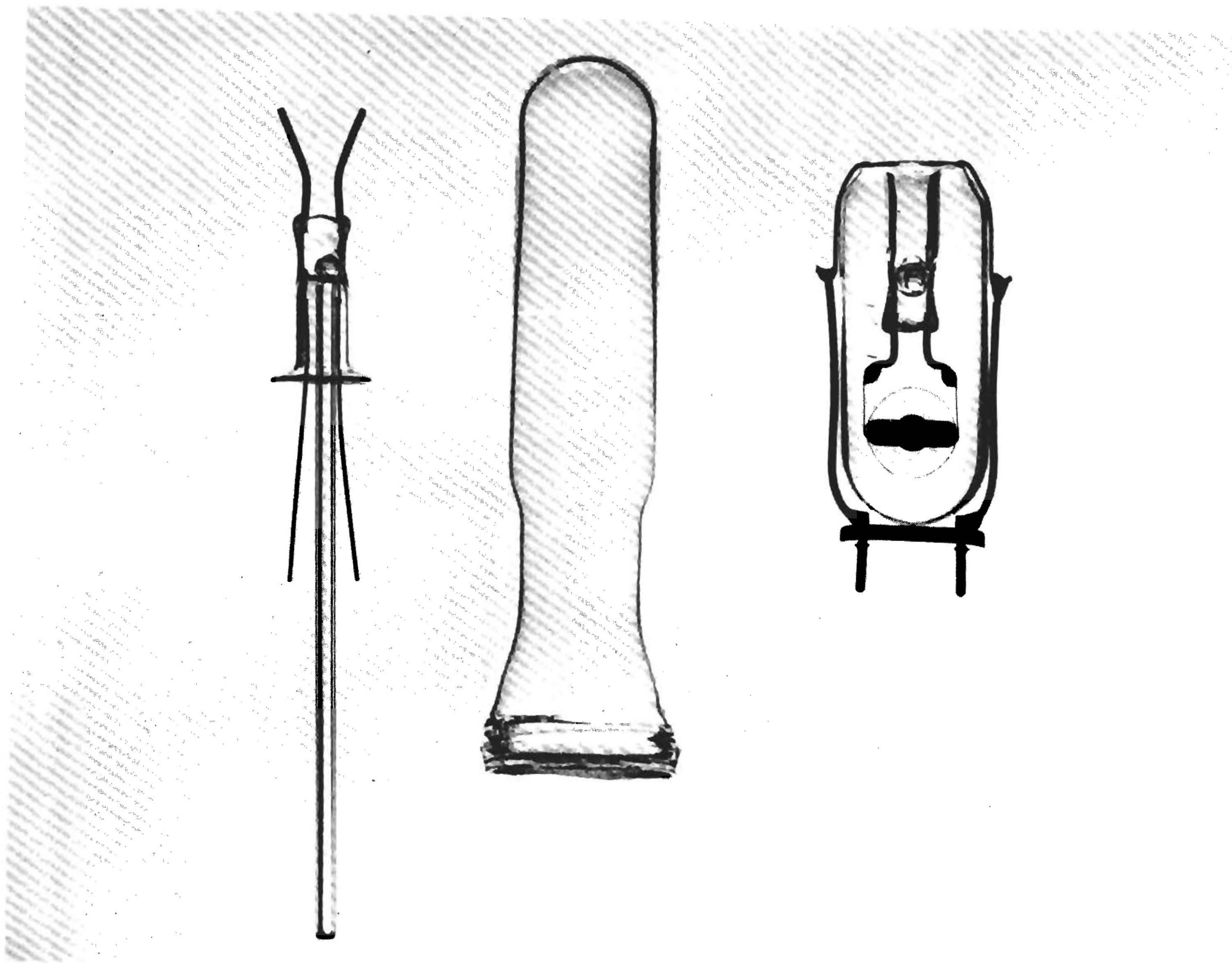


Figure 2. Glass Envelope and Stem Used as Container Assembly for Quartz Resonator.

C. RESONATORS FABRICATED AND EXAMINED

Approximately 250 resonators have been fabricated during the course of this contract. These consisted of the following general categories.

Blank Coating		Reclaimed Blanks	New Blanks	Total
Overcoating	gold + gold (20 in glass) gold + nickel (21 in glass)	39	37 21	76 21
Deplating	gold - gold	20	--	20
Base coat only	gold (18 in glass)	--	58	58
Base coat only	aluminum (25 in glass)	20	45	65
Base coat only	silver (none in glass)	--	10	10
			Total	250

Total in glass containers: 94

Total in mc HC-6/U containers: 156

Units were stored in a constant temperature oven at 85°C and their frequencies were measured daily during the first 14 days; thereafter measurements were made every 3 or 4 days. Periods of examination were from 60 to 180 days.

Characteristic patterns of behavior are exhibited in Figures 3-11 and 13-23. The description of each resonator is included on its frequency data plot.

D. ANALYSES OF DATA

1. Gold Plated Resonators Overplated with Evaporated Gold

In Figures 3-5 may be seen the stabilities obtained with units subjected to overcoating and mounted in glass containers. No significant directional drifts were observed for these units in operating periods up to 150 days. A reclaimed blank was used for unit Au 248 but new blanks were used for Au 255 and Au 261.

Relatively stable performance is also exhibited by units Au 96 and Au 179 of Figures 6 and 7. Only random frequency shifts were observed in 120 to 180 days. These were related to instrumental and personal measurement errors during the early period of the project in which a number of equipment modifications were made.

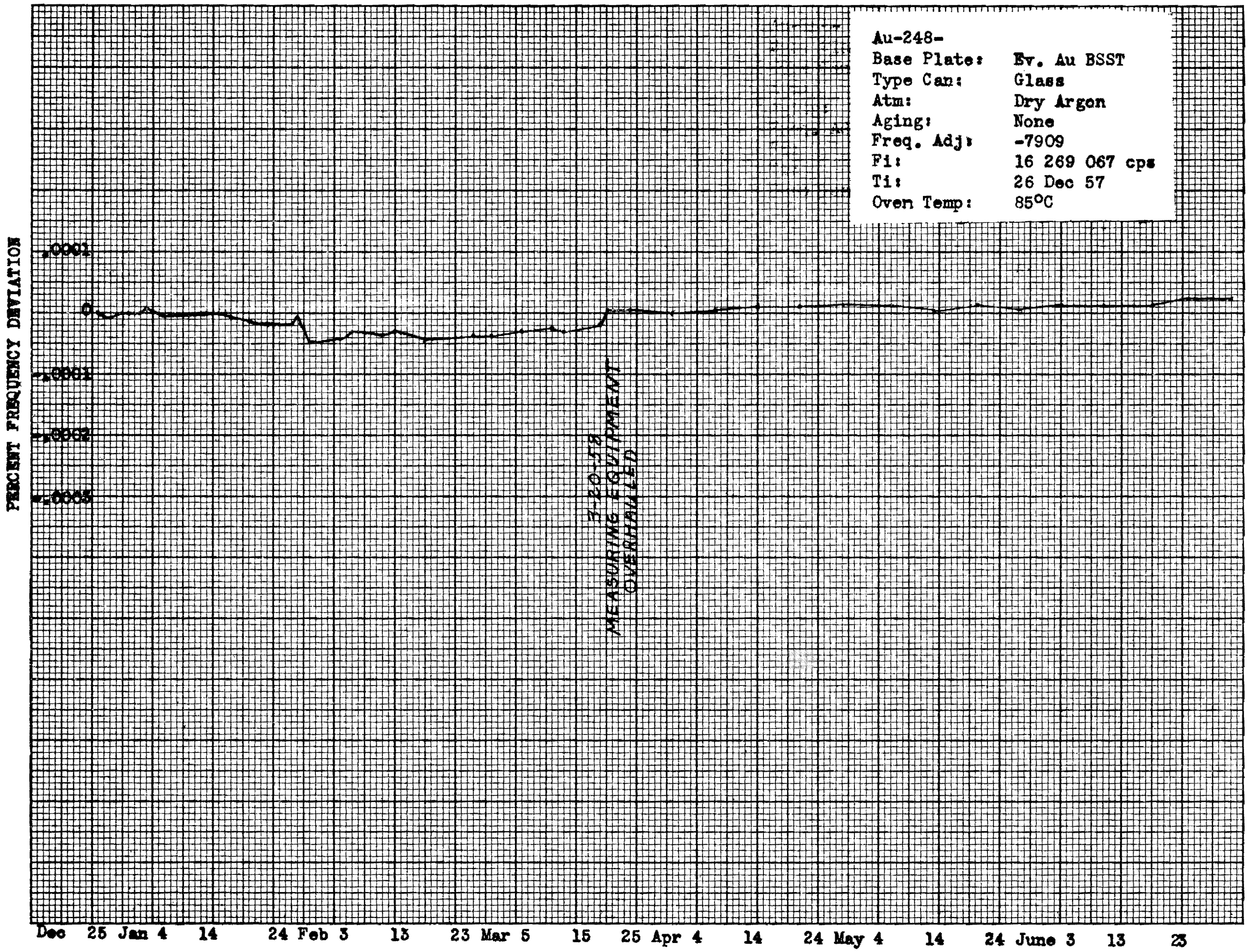


Figure 3. Plot of Frequency Data for Resonator Au-248. Overcoated, Glass Container, R_s, 5.5 ohms.

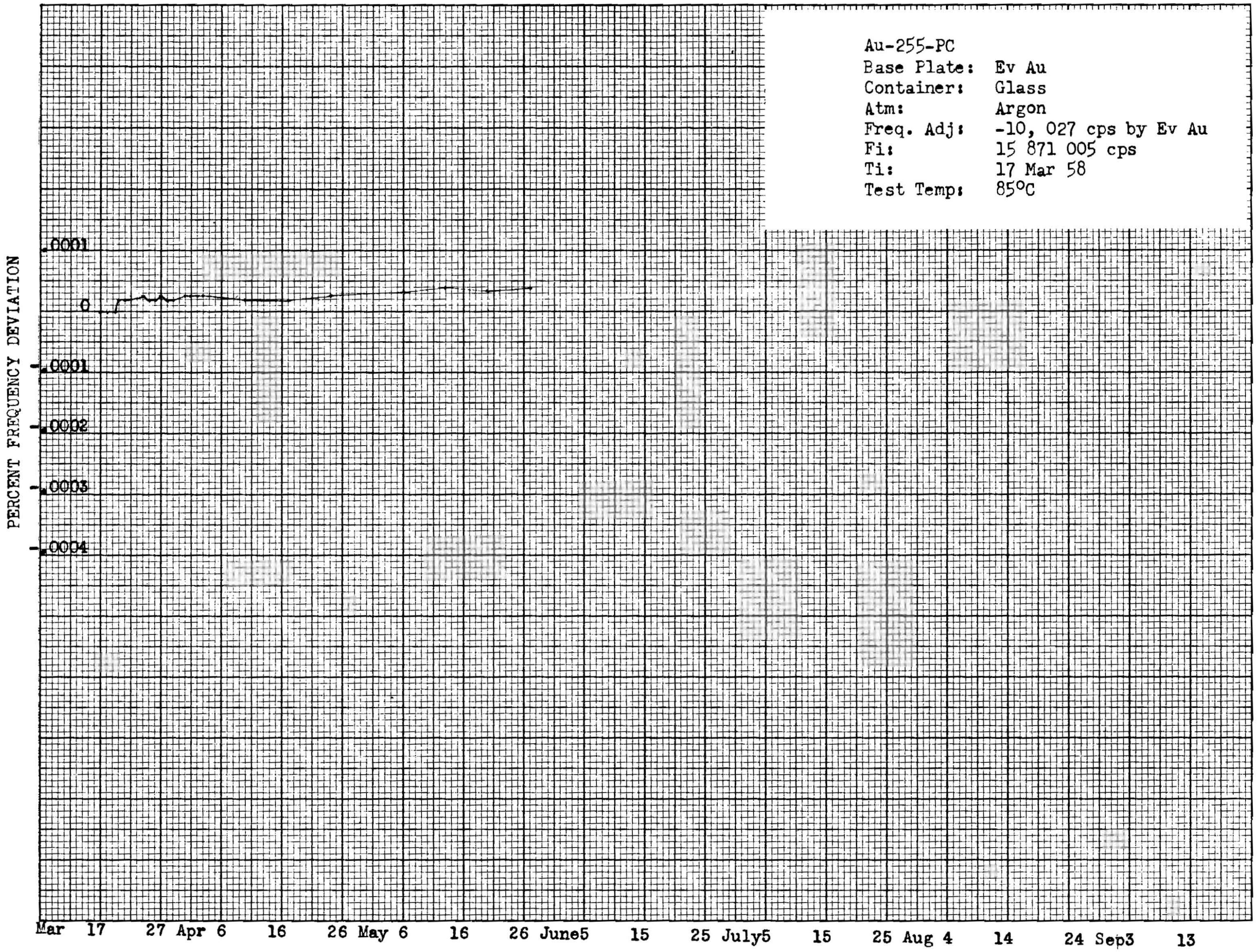


Figure 4. Plot of Frequency Data for Resonator Au-255. Overcoated, Glass Container, R_s, 5.2 ohms.

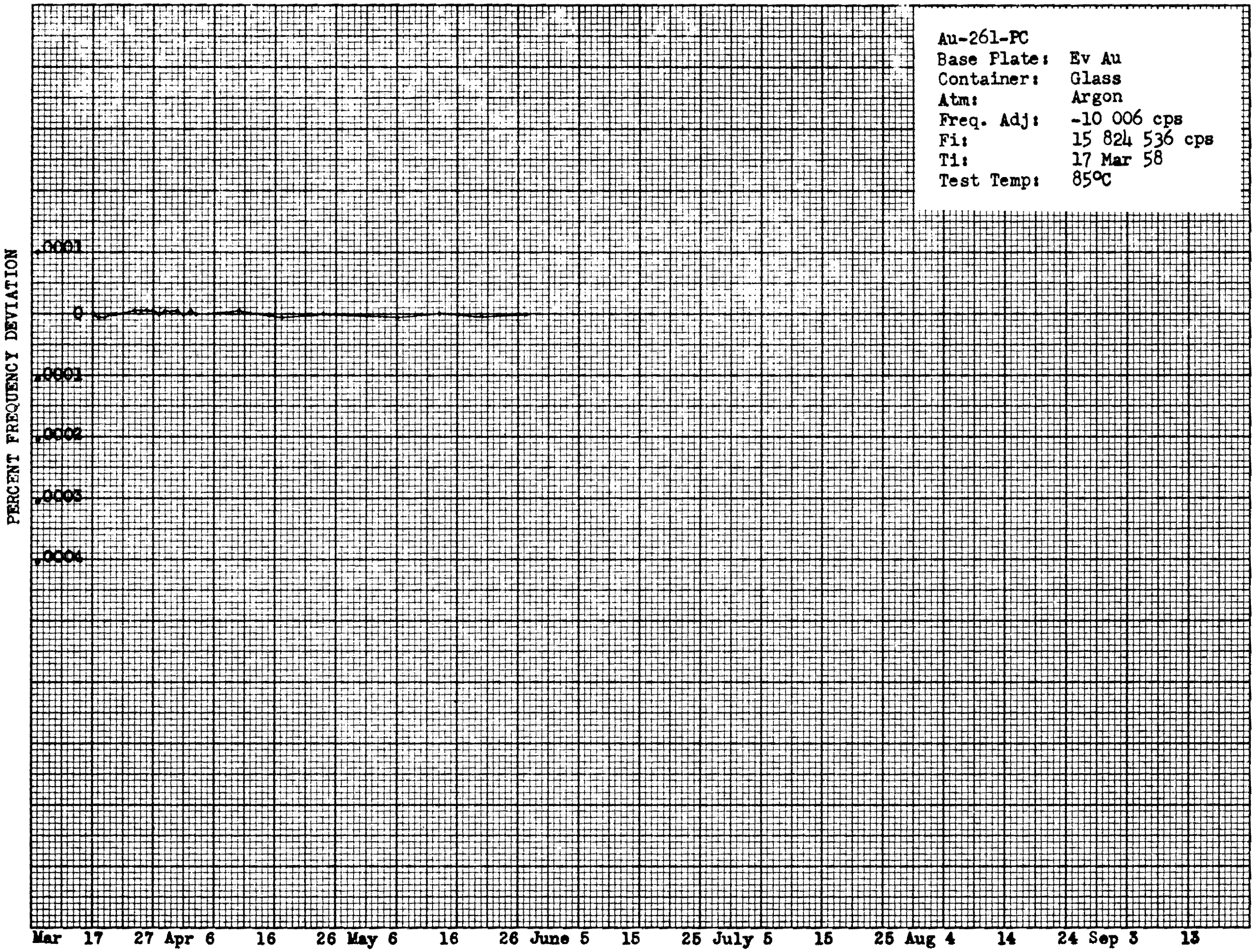


Figure 5. Plot of Frequency Data for Resonator Au-261. Overcoated, Glass Container, R_s, 5.5 ohms.

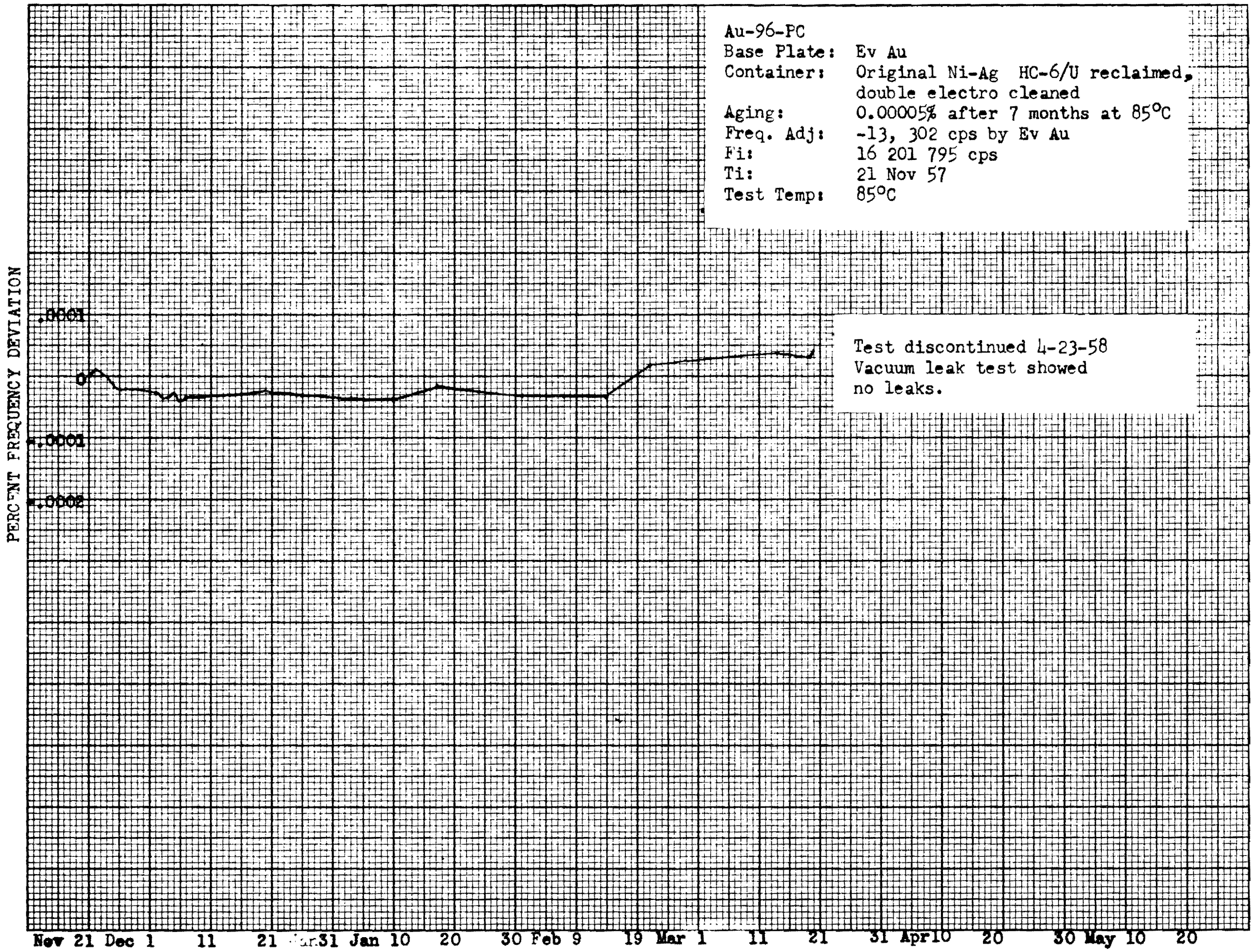


Figure 6. Plot of Frequency Data for Resonator Au-96. Overcoated, Glass Container, R_s, 4.5 ohms.

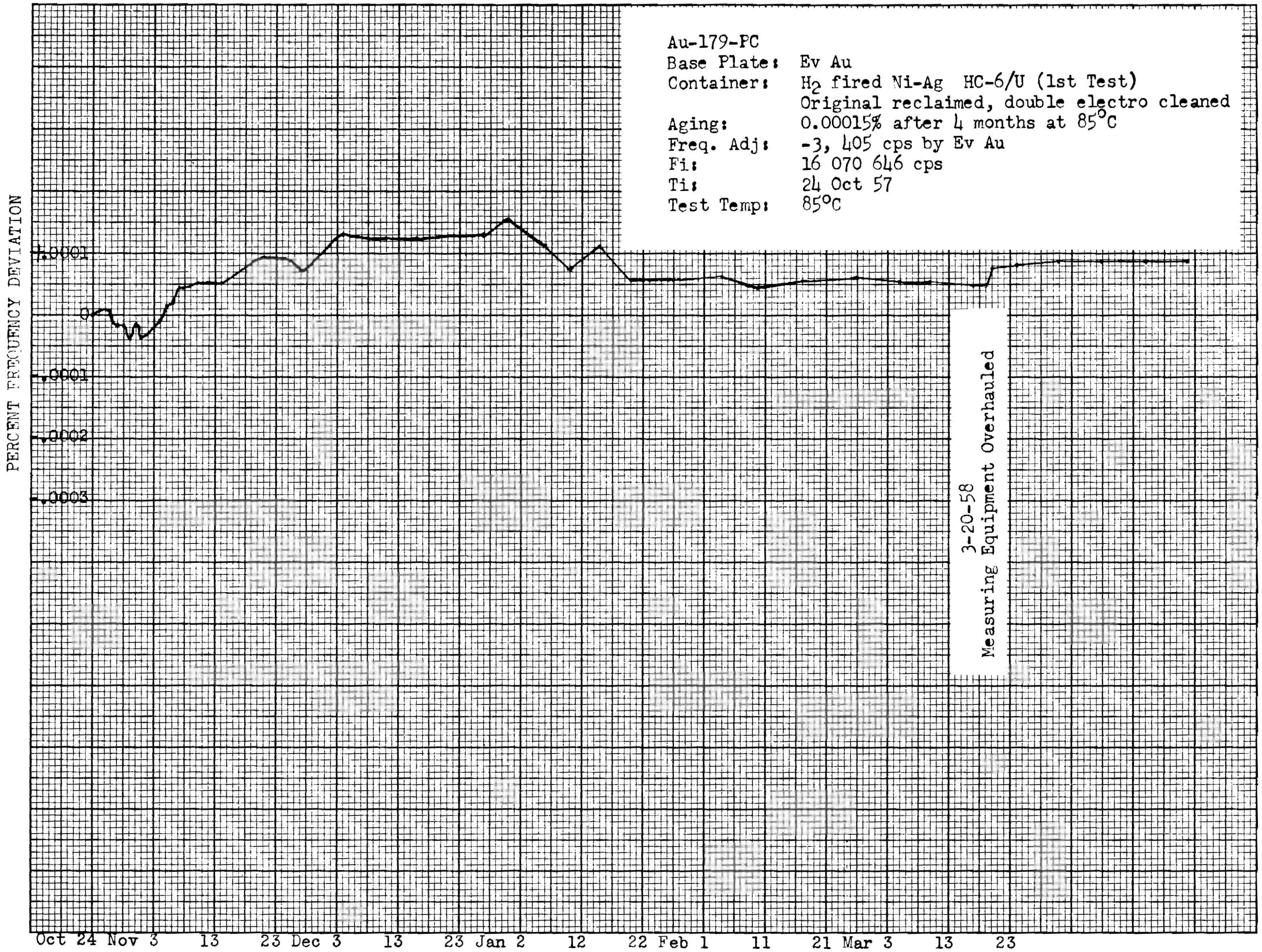


Figure 7. Plot of Frequency Data for Resonator Au-179. Overcoated, HC-6/U Container, R_s, 6.0 ohms.

In contrast to the relatively stable performance of the foregoing units Figure 8 depicts the behavior of a unit which had a slight leak according to the vacuum leak test described. Since a large number of the units exhibited plots similar to this or with greater negative frequency drifts, all units were subsequently examined for leaks. In general drifts of this nature were correlated with units shown to have slow leaks.

2. Gold Plated Resonators Deplated by Ion Bombardment

Units deplated by ion bombardment exhibited markedly less stable frequency characteristics than the units just described. In Figure 9 may be seen the frequency pattern exhibited by a resonator before bombardment and in Figure 10 may be observed its pattern after frequency adjustment by bombardment, remounting and measurement. A marked degradation of frequency stability occurred for all units.

Although many of the units subjected to deplating were subsequently found to be leakers, three did not leak when tested by the vacuum leak test. The bases of all save one (Au 194) did exhibit small cracks. However, it does not appear that all units would exhibit similar type stability plots, except for some variation in the slope rate, unless there was a significant degradation effect resulting from the bombardment.

A suggested explanation of the observed degradation is the deposit of a foreign metal by the bombardment action. This metal may have subsequently alloyed with the gold plating and increased the plating thickness and therefore the moment of inertia of the vibrating system. The true effect on stability of deplating by ion bombardment, however, can only be established after further and more carefully conducted frequency adjustments in which the quartz face is protected from contamination to the degree practicable. Markedly smaller adjustments made by this method appear less likely to show significant degradatory influences.

3. Gold Plated Resonators Deplated by Tesla Discharge Coil

Frequencies of gold plated resonators can be adjusted upward by plating removal with the discharge from a hand guided Tesla Discharge Coil similar to those frequently used for cleaning purposes. Gold and aluminum plating may be removed but silver plating will be oxidized by ozone generated during the discharge. However, the discharge is difficult to control and frequency changes of several thousand cycles induced by this method resulted

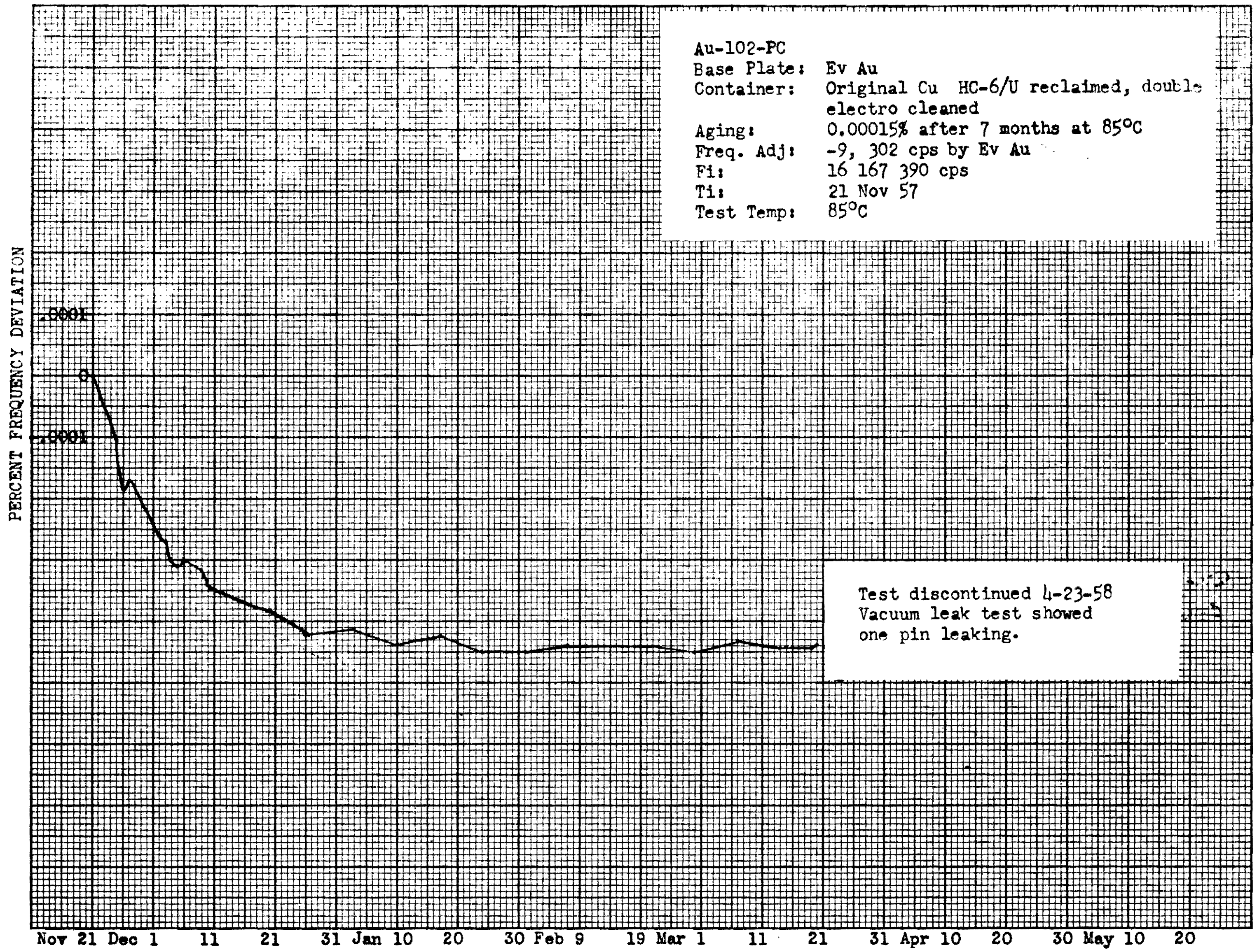


Figure 8. Plot of Frequency Data for Resonator Au-102. Overcoated, HC-6/U Container, R_s, 4.0 ohms.

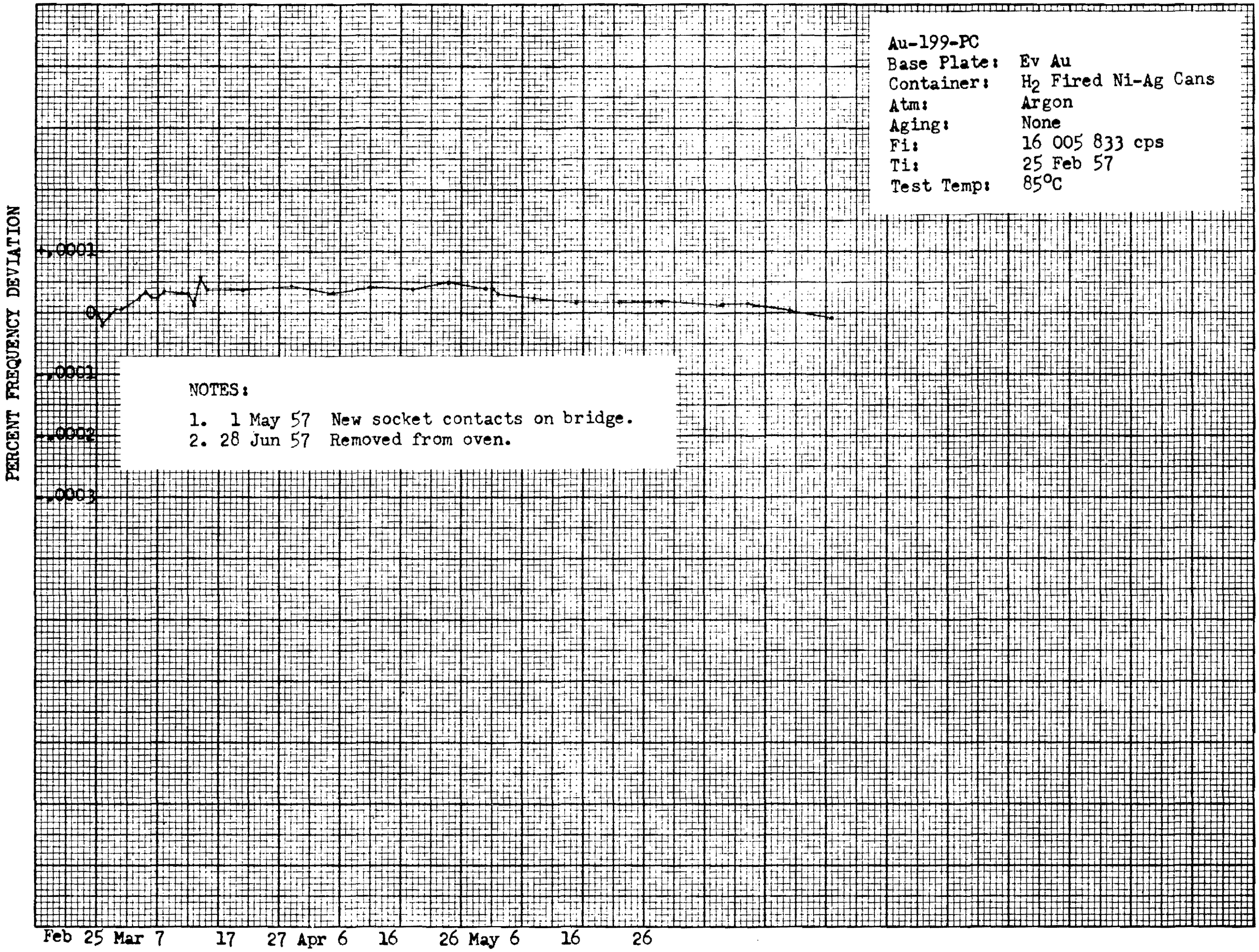


Figure 9. Plot of Frequency Data for Resonator Au-199. Not Overcoated, HC-6/U Container, R_s, 4.0 ohms.

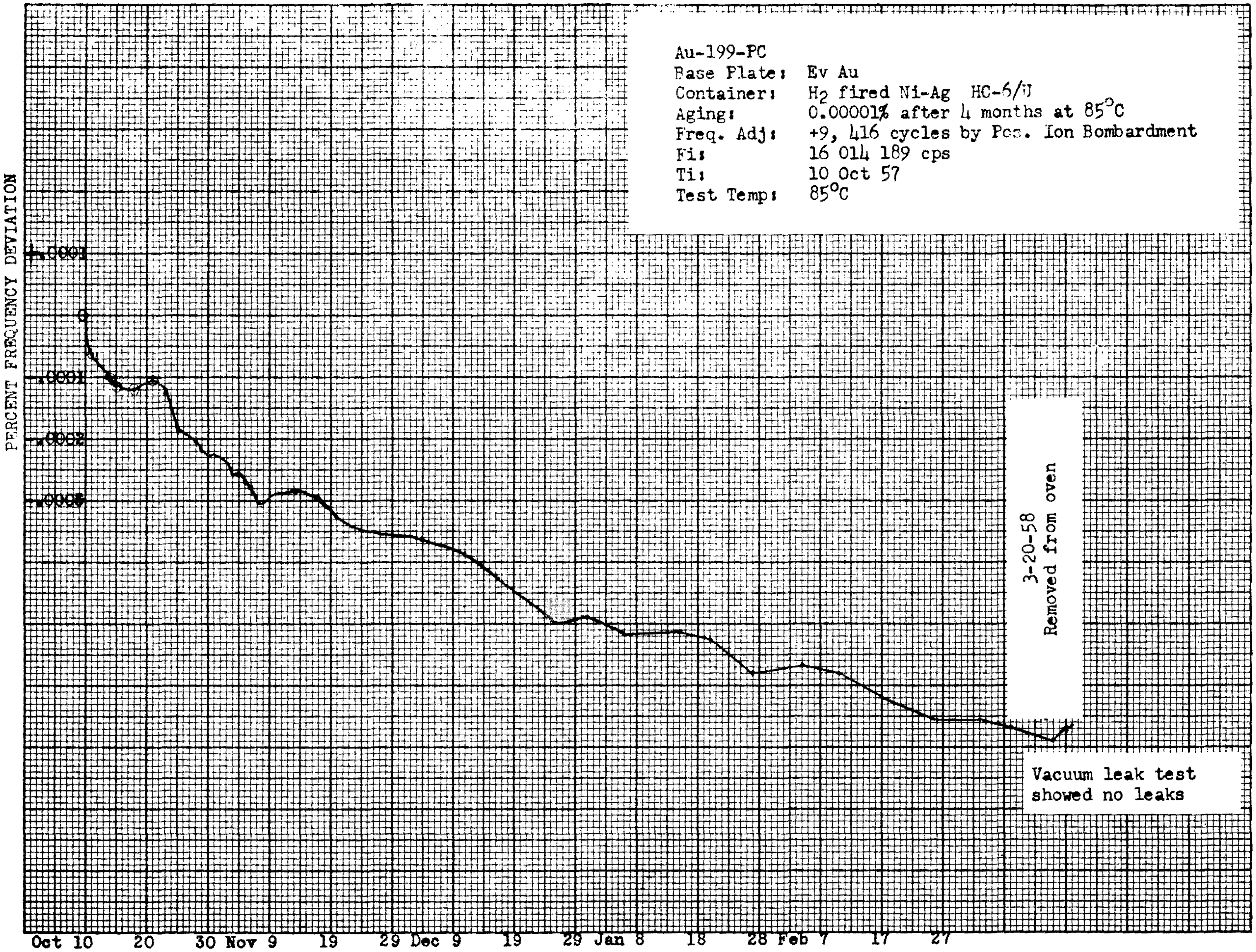


Figure 10. Plot of Frequency Data for Resonator Au-199. Deplated, HC-6/U Container, R_s, 5.5 ohms.

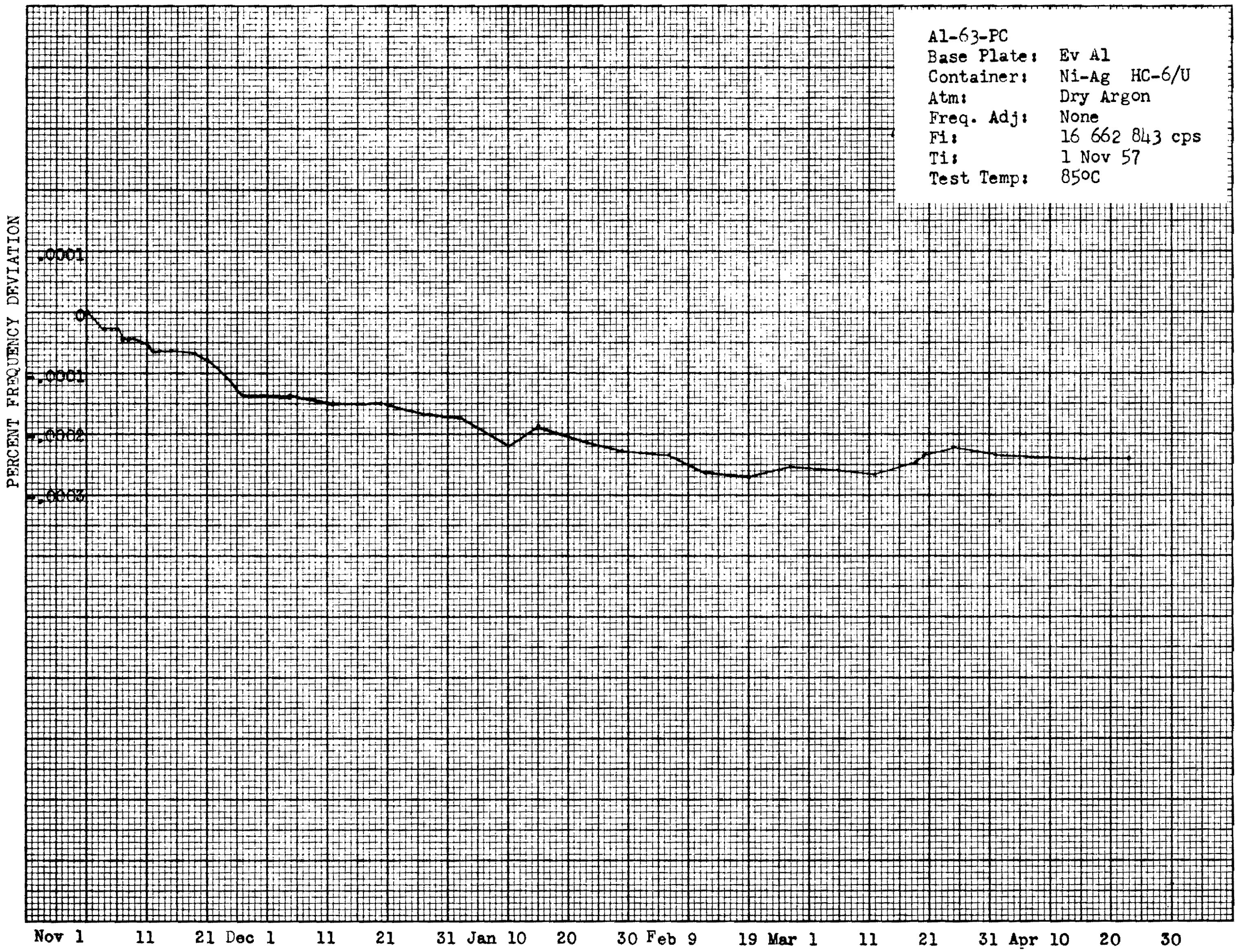


Figure 11. Plot of Frequency Data for Resonator A1-63. Not Overcoated, HC-6/U Container, R_s, 9.5 ohms.

The second set of units made at a much later date, with every precaution exercised to prevent leaking, initiated by base cracking, exhibited similarly rapid drops in frequency of 2 to 4 parts per million during the first 30 days of operation. Leveling off of the stability curves was noted in most instances toward the end of the period of measurement, forty days.

One observation that appeared significant was an upward drift registered after a period of 100 days by several units. A typical upward drift is exhibited in Figure 12 (Al 66). It appears to be the result of an R_s increase. Similar increases in frequency occurred for several units concurrently with increases of R_s. As corrosion progresses, especially for units with thinner films, it is conceivable that R_s values may appreciably increase. Such increases are almost invariable accompanied by frequency increases.

As a result it is suggested that R_s values for aluminum units should be plotted on the same graph with the stability data and account taken of the influence of changes in this parameter in interpretation of the frequency data. The sometimes anomalous behavior of aluminum plated units may be partially clarified by consideration of this upward frequency vector opposed to the normal downward drift encountered due to corrosion or adsorption phenomena.

5. Silver Plated Resonators Not Overplated

A series of ten silver plated units were prepared in the normal manner by evaporation of the silver base coat onto the hot quartz blanks maintained at a temperature of about 200°C. Since these units were fabricated after the discovery of the high incidence of base cracks every precaution was taken to prevent further occurrence of this defect. Although the units were mounted in the HC-6/U cans these resonators gave excellent stabilities over the limited period of life (50 days) as shown by the plot of resonator E-4 in Figure 13.

6. Other Measurements

A number of other measurements were made. These included studies of resonators, base coated only with evaporated gold on the hot quartz blank and mounted in the new type glass envelope, sealed in vacuo or in residual atmospheres of dry argon or dry nitrogen. The stabilities of the units in vacuo appeared slightly superior to the others but only one unit showed any appreciable drift in 30 days. This one appeared to be an obvious leaker since it dropped rapidly to -0.0008 percent in less than 30 days. Four of the others

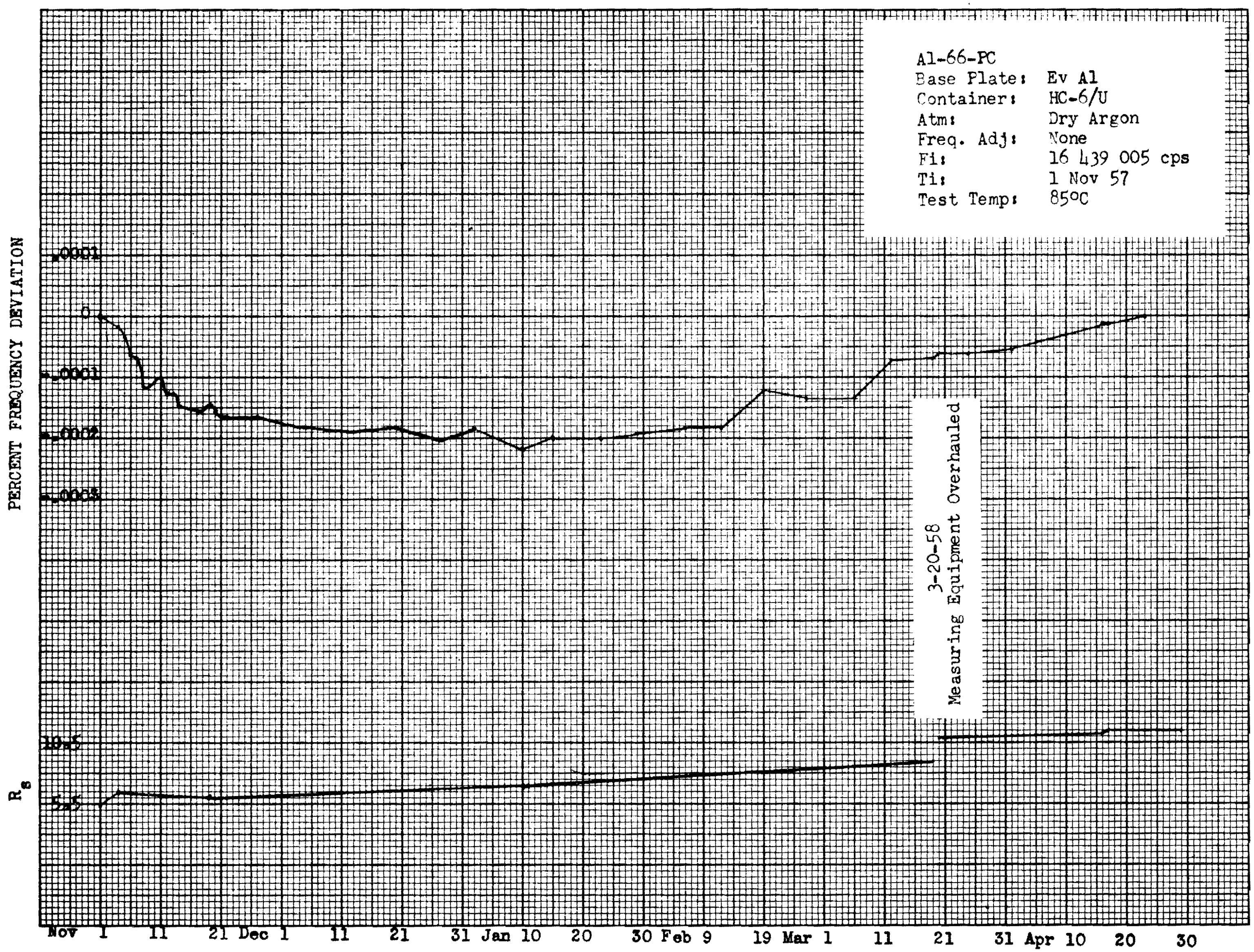


Figure 12. Plot of Frequency Data for Resonator Al-66. Not Overcoated, HC-6/U Container, R_s, 11.5 ohms.

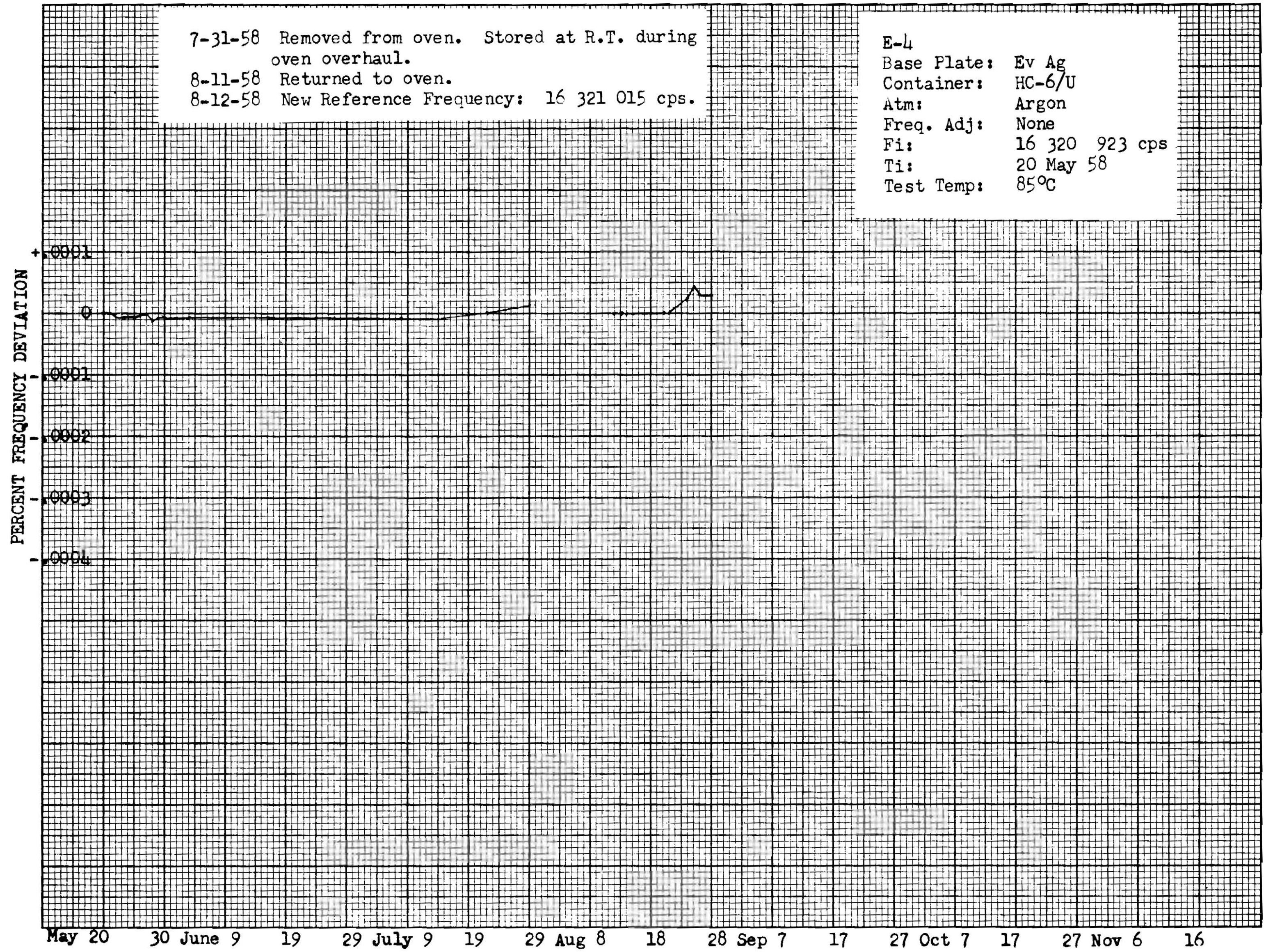


Figure 13. Plot of Frequency Data for Resonator Ag-E-4. Not Overcoated, HC-6/U Container, R_s, 6.0 ohms.

showed departures as high as 0.0005 percent in the 30 day period but nine were within ± 0.0003 percent departure in the 30 day period. None of the latter showed definite directional tendencies.

One group of base plated gold units (series D-1 to D-10) were adjusted to frequency by evaporating the overcoating gold at a relatively high pressure, 10^{-3} mm of mercury instead of the 10^{-5} mm previously considered the best practice. This particular series was among those showing a high percentage of leaks. Unit D-4 of Figure 14 exhibited superior stability over its 30 day test period. The others showed greater negative drifts. However, results were inconclusive as to the actual effect of the higher pressure used during the frequency adjusting step.

A second group of gold plated units, CR-1 to CR-7 base plated only, were mounted with 10 mil diameter spring clips instead of the 6 mil diameter type previously used. These units, in general, showed a sharp upward frequency drift of as much as + 0.0003 percent during the first 30 day period. Only the units subsequently proved to be leakers showed horizontal or negative frequency plots. The upward shift is ascribed to mechanical stresses applied to the quartz blanks by the 10 mil diameter clips. These spring clips were so rigid that proper alignment was difficult to obtain and the crystal blank was not free of stress from this source.

7. Leaks in the HC-6/U Container

As previously mentioned the unexpected instability of many resonators fabricated by methods known to give excellent stability led to a search for a cause of the observed frequency drifts. Since many units exhibited patterns of frequency behavior typical of that shown by known leakers all units under examination were removed from the oven and inspected with a stereomicroscope. This inspection revealed cracks about the pins of nearly every HC-6/U base (made of a fired ceramic compound). Typical cracks are shown in Figure 15 A.

Similar cracks could be formed by pressing the pins of a new base slightly toward each other with a pair of pliers. Insertion of the resonator in the new and tight ceramic sockets, recently installed in the oven, damaged many units in a pattern similar to that shown in Figure 15 A. Although the set of bases used may have been a poor batch it is probable that damage must often occur to resonators in industry and in the field from insertion in poorly fitting sockets.

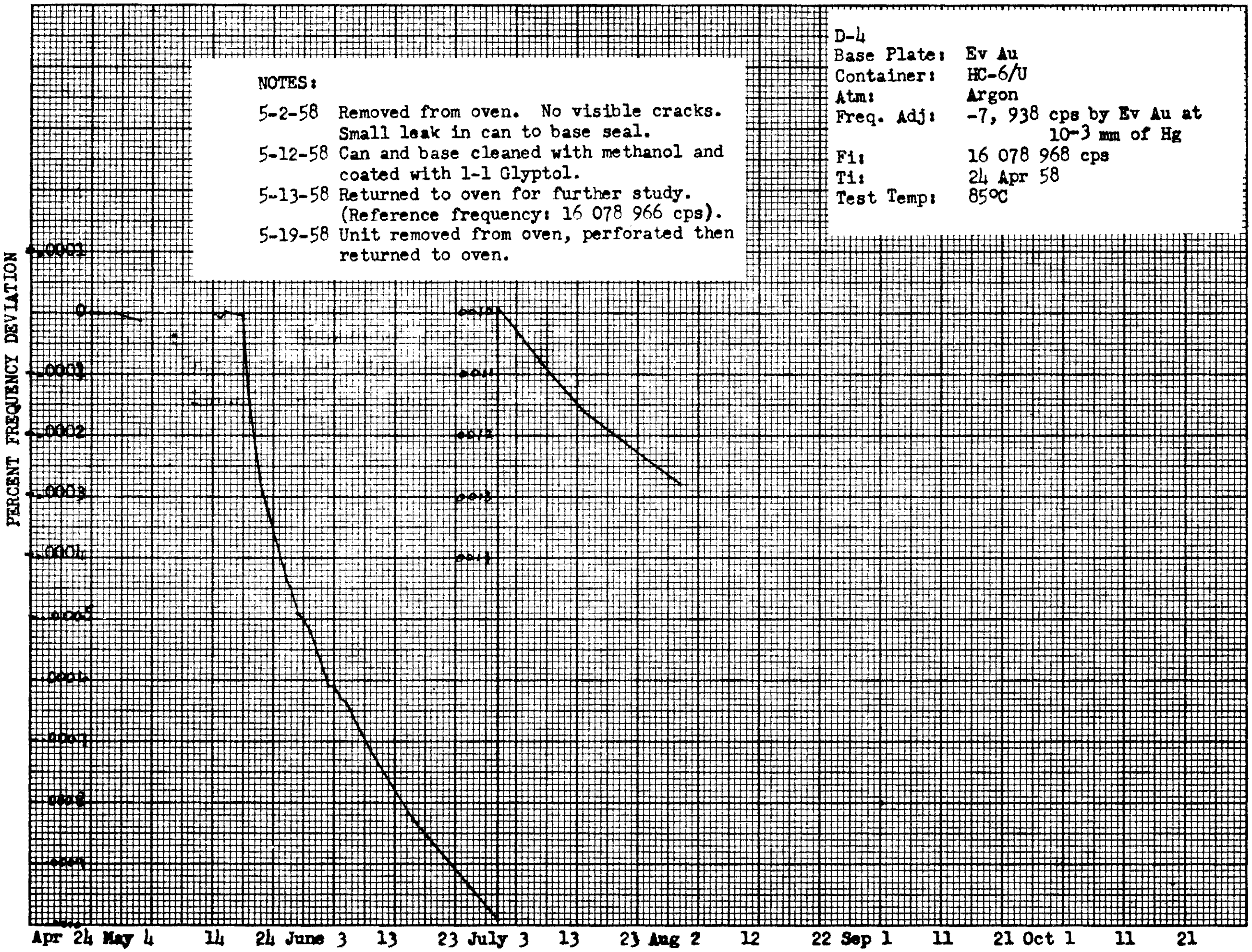
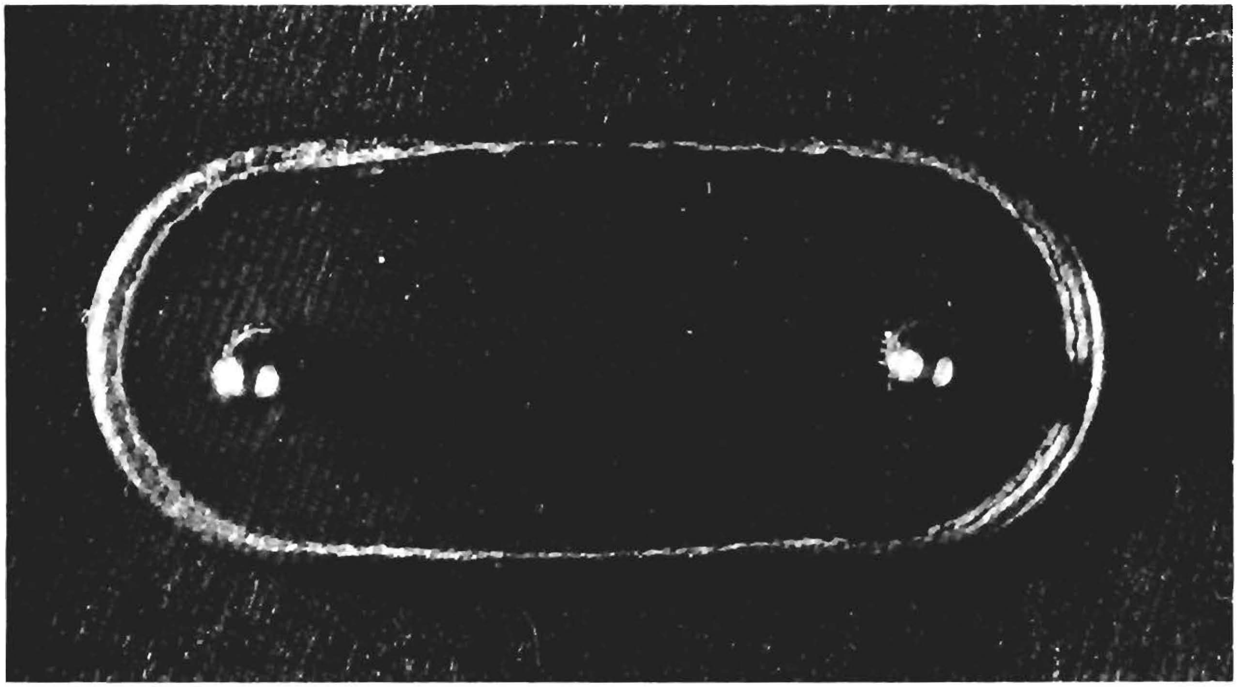
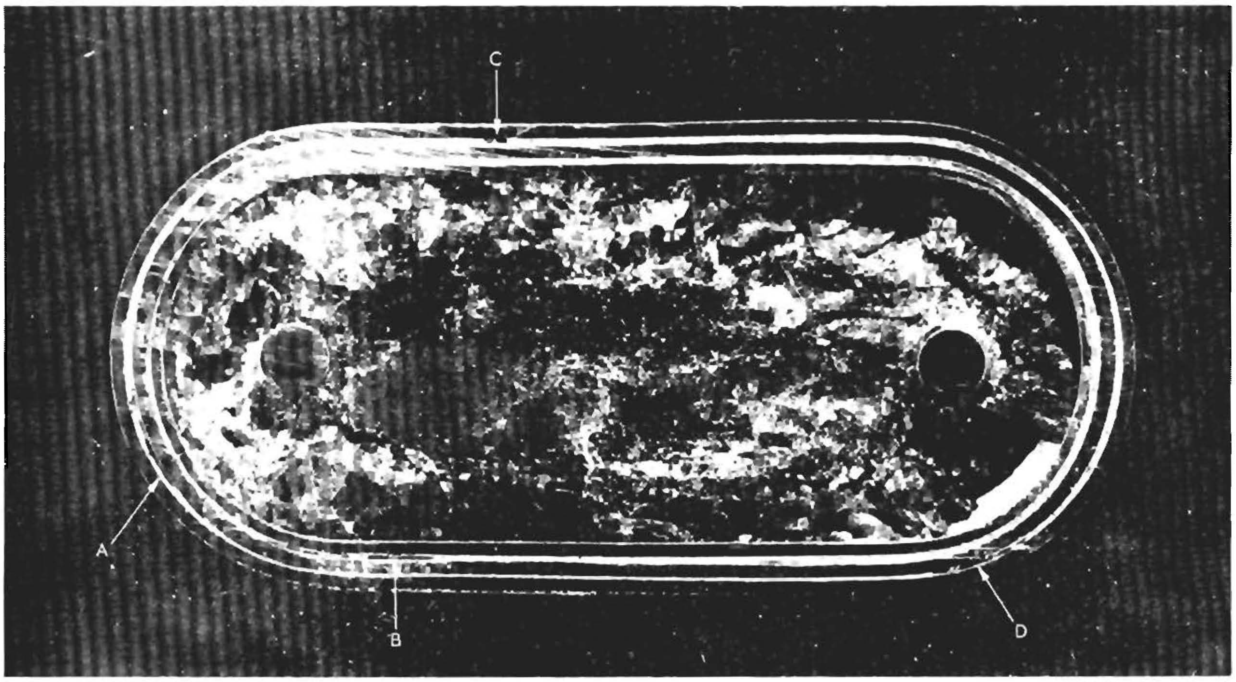


Figure 14. Plot of Frequency Data for Resonator Au-D-4. Overcoated, HC-6/U Container, R_s, 5.6 ohms.



A. CRACKS FORMED BY STRESSING PINS.



B. IMPERFECT SOLDER SEALS.

Figure 15. Micrographs of Bases of the HC-6/U Container Showing Potential Leaks.

Of the resonators examined, 92 percent were shown to have cracks in the base. Subsequent examination of these units by the vacuum leak test disclosed that the bulk of these units were leakers of varying rates. Many leaks were located near the pins and a few were noted along the rim and in the final seal. These leaks were not disclosed by hot water leak tests of the units just prior to insertion in the oven. Some of the leaks revealed by the test were undoubtedly inactive during the frequency measurement period since the 15 lbs pressure differential between the interior and exterior of the can probably opened leaks that did not exist under zero pressure differential. Glyptal coating of the cans after fabrication, as performed, undoubtedly closed many small leaks that would normally have been active. In general the downward drift rate of the units corresponded to the size of the leaks exposed.

Subsequent to the discovery of the numerous leakers, units of excellent stability coated with gold, aluminum or silver, were intentionally punctured. The smallest leak that could be produced by pressure with a very fine needle was large compared with the leaks previously discussed. All units underwent rapid downward frequency shifts of 10 or more parts per million within a few days. In Figures 14 and 16 may be observed the behaviors of punctured units.

The danger of leaks in the HC-6/U container is a constant one and may readily occur at a time subsequent to inspection and approval of a given unit. Gaps in the solder seal of a typical HC-6/U can are shown in the micrograph of Figure 15 B displaying a section through the seal parallel to the base. Arrows indicated defective areas. This seal appeared good on visual examination only. The innocuous appearing operation of inserting the unit in a socket is a case in point. Certainly sockets should be designed with tolerance sufficient to eliminate this danger and bases should be designed to accept a certain degree of abuse. On the other hand, the resonator sealed in glass appears to be the only sure cure for post fabrication leak development.

8. Resonators Made Subsequent to 1 June 1958

a. Units Fabricated

As reported, numerous leakers among the resonators fabricated and examined previous to the 12th Annual Frequency Symposium, 6-8 May 1958, clouded the interpretation of a large portion of the data obtained. Furthermore,

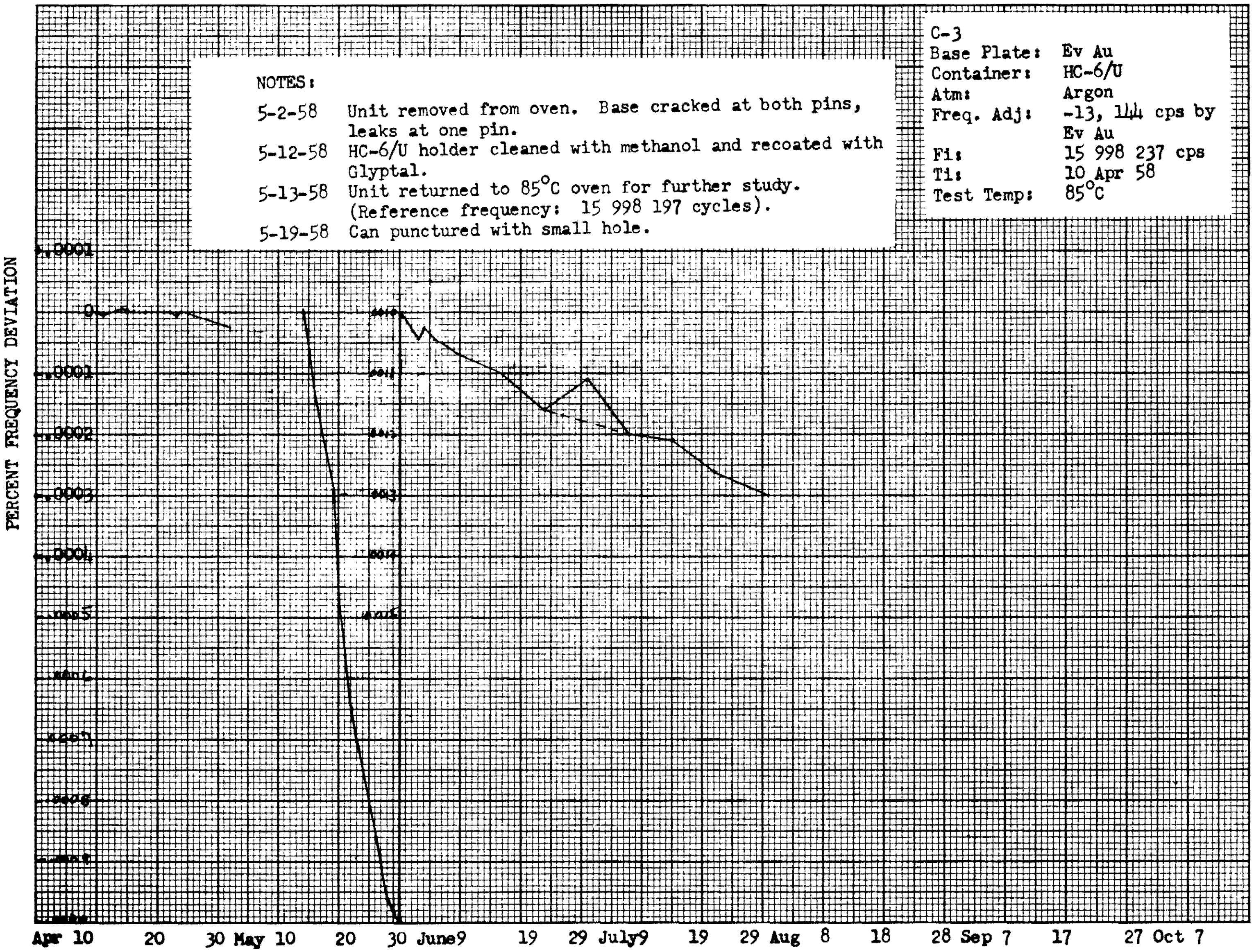


Figure 16. Plot of Frequency Data for Resonator Au-C-3. Overcoated, HC-6/U Container, R_s, 5.7 ohms.

there remained to be studied the effects on stability of overcoating to frequency by electroplating. As a result, a number of new studies were undertaken; these included the following resonator groups receiving the stipulated treatments.

Group Number	No. of Units	Plating and Processing	General Comment
Gold Base Plated Only			
G1 - G6	5	Ev Gold Base Plate Only, Glass Container. Vacuum Sealed.	4/5 stable
H1 - H7	6	Ev Gold Base Plate Only, Glass Container. Argon Atmosphere.	3/6 stable
I3 - I5	3	Ev Gold Base Plate Only, Glass Container, Nitrogen Atmosphere.	3/3 stable
Gold Plus Electroplated Gold			
L1 - L6	5	Ev Gold plus El Gold, Glass Container. Vacuum Sealed.	4/5 stable
Gold Plus Electroplated Nickel			
J1 - J10	10	Ev Gold Base plus El Nickel, Glass Container. Vacuum Sealed.	5/10 stable five had high positive drifts
K2 - K6	5	Ev Gold Base plus El Nickel, Glass Container. Vacuum Sealed.	0/5 stable all positive drifts
Gold plus Evaporate Nickel			
O1 - O7	6	Ev Gold Base plus Ev Nickel, Glass Container. Vacuum Sealed.	4/6 stable only short test period, somewhat erratic
Evaporated Aluminum, Base Plate Only			
F1 - F10	10	Evaporated Aluminum, Base Plate Only, HC-6/U Container, Ni-Ag, Argon Atmosphere	All units registered -0.0002% or more decrease in frequency in 60 days.
M1 - M6	6	Evaporated Aluminum, Base Plate Only, Glass Container Vacuum Sealed.	All units registered -0.0002% or more decrease in frequency in 60 days.

Group Number	No. of Units
Evaporated Aluminum, Base Plate Onl	
$M_1 1$ - $M_1 7$	7
N1 - N6	6
$N_1 1$ - $N_1 6$	6
Total Resonators:	75

b. Resonators Base Pla

Generally speaking the agreed with that previously presente 17 gives a result typical of the Gro evaporated gold and sealed in glass c the atmosphere of sealing, i.e., vac Although there was little difference number of units in the gaseous atmos which wer inexplicable. Since the en nitrogen trap there was a possibility ant entered the unit on admitting the ties exhibited by the gas filled unit ascribed to a contaminant included in

c. Resonators Base Plat

Likewise the data obtain coated units are in agreement with th resonators of the F, M, M_1, N, and N_1 N1 - 6 were data obtained that were s

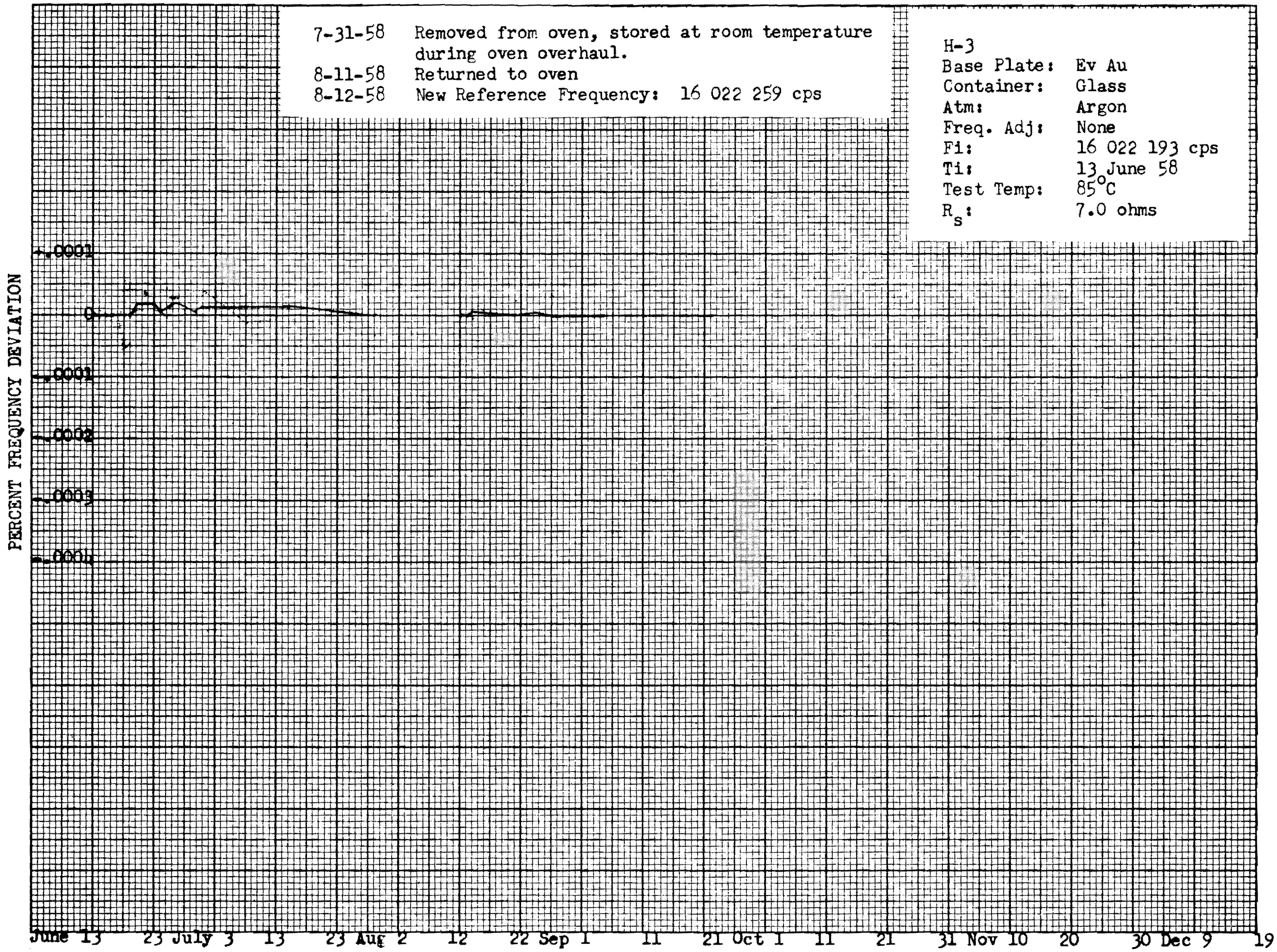


Figure 17. Plot of Frequency Data for Resonator Au-H-3. Not Overcoated, Glass Container.

obtained for aluminum units. A typical pattern is shown in Figure 18 (M_1-4) and an exceptional one in Figure 19 (M_1-7). These units were distinguished from the others by the fact that the plated blanks were aged in air at 450°C prior to mounting and were stored 12 days at room temperature before being placed on test at 85°C. A group receiving similar treatment, except for the 12 days aging period before testing, gave rapid downward drifts during the initial few days on test. The N group which were base plated on quartz at 250°C and sealed without aging gave excellent stability as shown in Figure 20 (N-3).

A comparison of Figure 18 with Figures 11 and 12 for the preceding studies of resonators base plated with evaporated aluminum reveals the similarity of the findings. The data of Figures 19 and 20 are somewhat better than any obtained in preceding measurements at 85°C. Aluminum plating is intrinsically a less stable plating than gold and units may be expected in most cases to exhibit initial downward drifts of several parts per million even when sealed in glass containers. There may exist a meticulous processing technique which will consistently give stability values of the types shown in Figures 19 and 20 but a further search is required in order to verify whether the techniques used and the results obtained for these units are consistently repeatable.

d. Resonators Overplated with Electroplated Gold

Of particular interest are the experiments on overplating resonators to frequency by electroplating. Again it was shown that overplating gold with gold may be accomplished without degradation of frequency. This is clearly indicated in Figure 21 (L-6). The frequency of this unit was decreased by 186, 243 cycles by the overplating and the unit remained stable.

e. Resonators Overplated with Electroplated Nickel

In contrast to the behavior outlined above, gold plated resonators overplated with electroplated nickel exhibited rapid upward shifts in frequency as shown in Figure 22 (J-5). Units of the J group receiving the smaller plate-back exhibited the smaller frequency increases subsequently and the upward slope decreased with time. However, the K group, similarly fabricated, with plate-backs in the range 4000 to 12500 cycles, all exhibited major upward shifts.

In order to check whether this behavior was typical of overcoating with nickel or of electroplated nickel only, the O group overplated with evaporated nickel was prepared. The latter did not exhibit the rapid upward shift experienced by units of J and K groups. A typical frequency pattern is

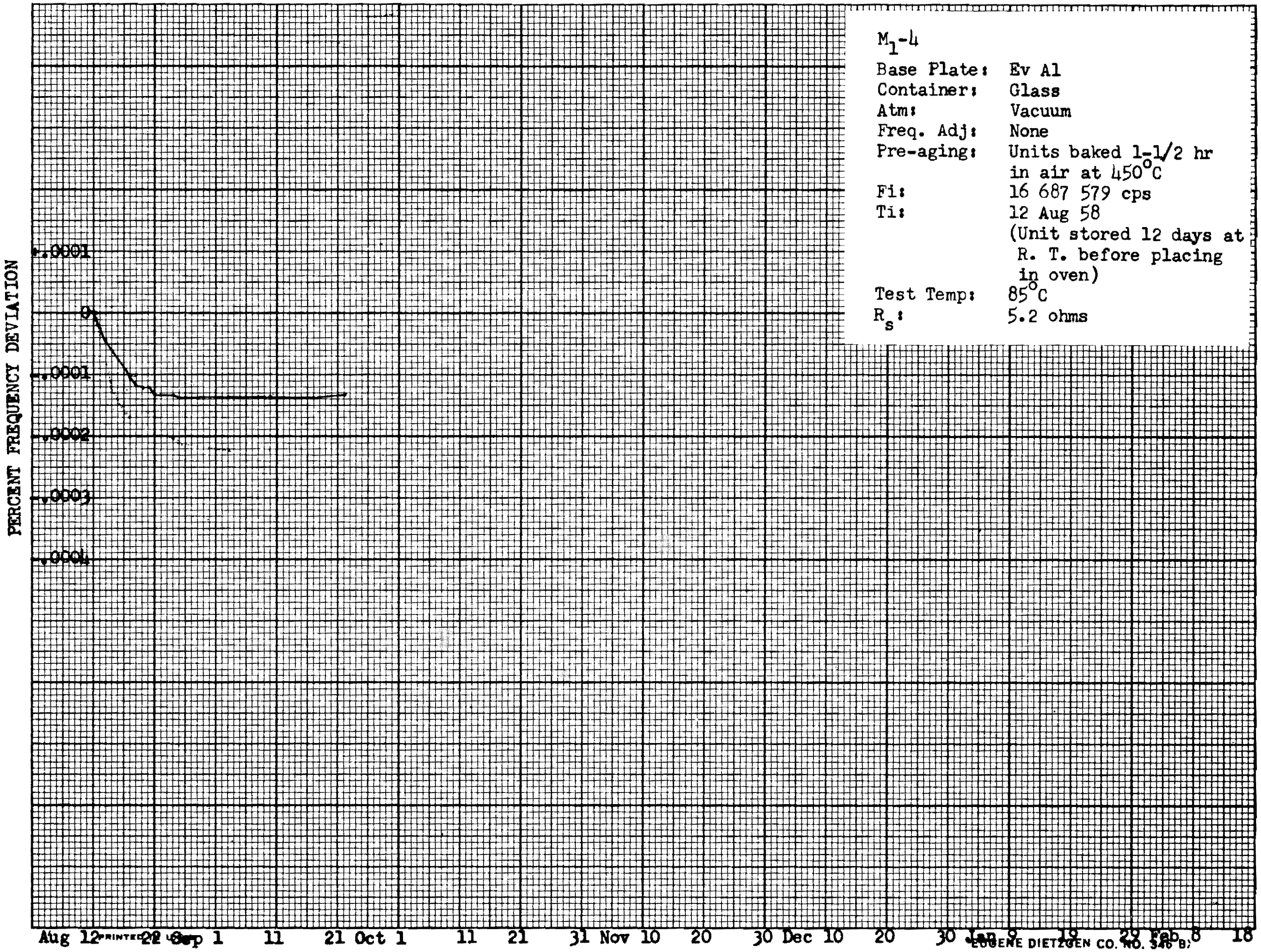


Figure 18. Plot of Frequency Data for Resonator Al-M_1-4. Not Overcoated, Glass Container.

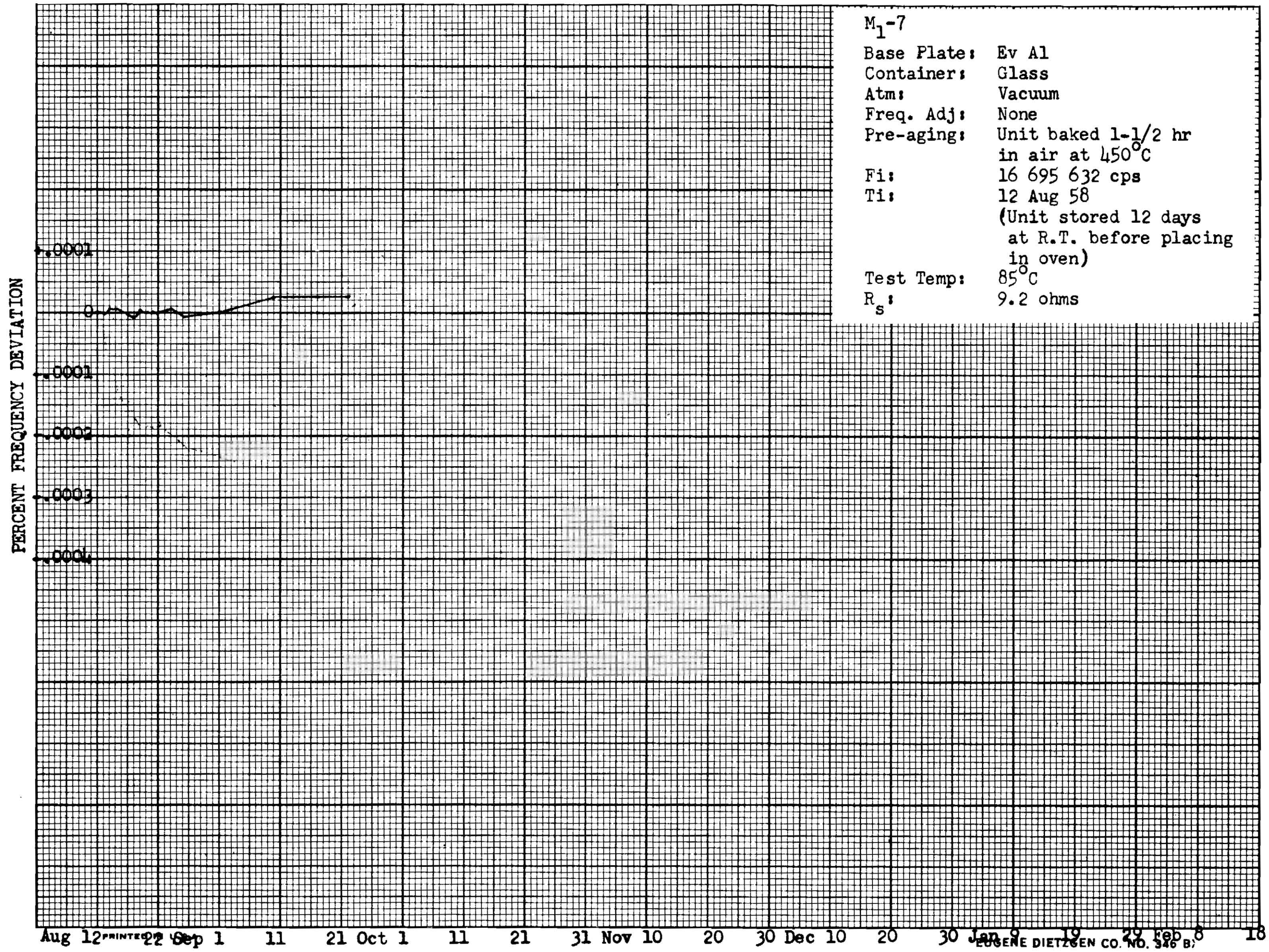


Figure 19. Plot of Frequency Data for Resonator Al-M_1-7. Not Overcoated, Glass Container.

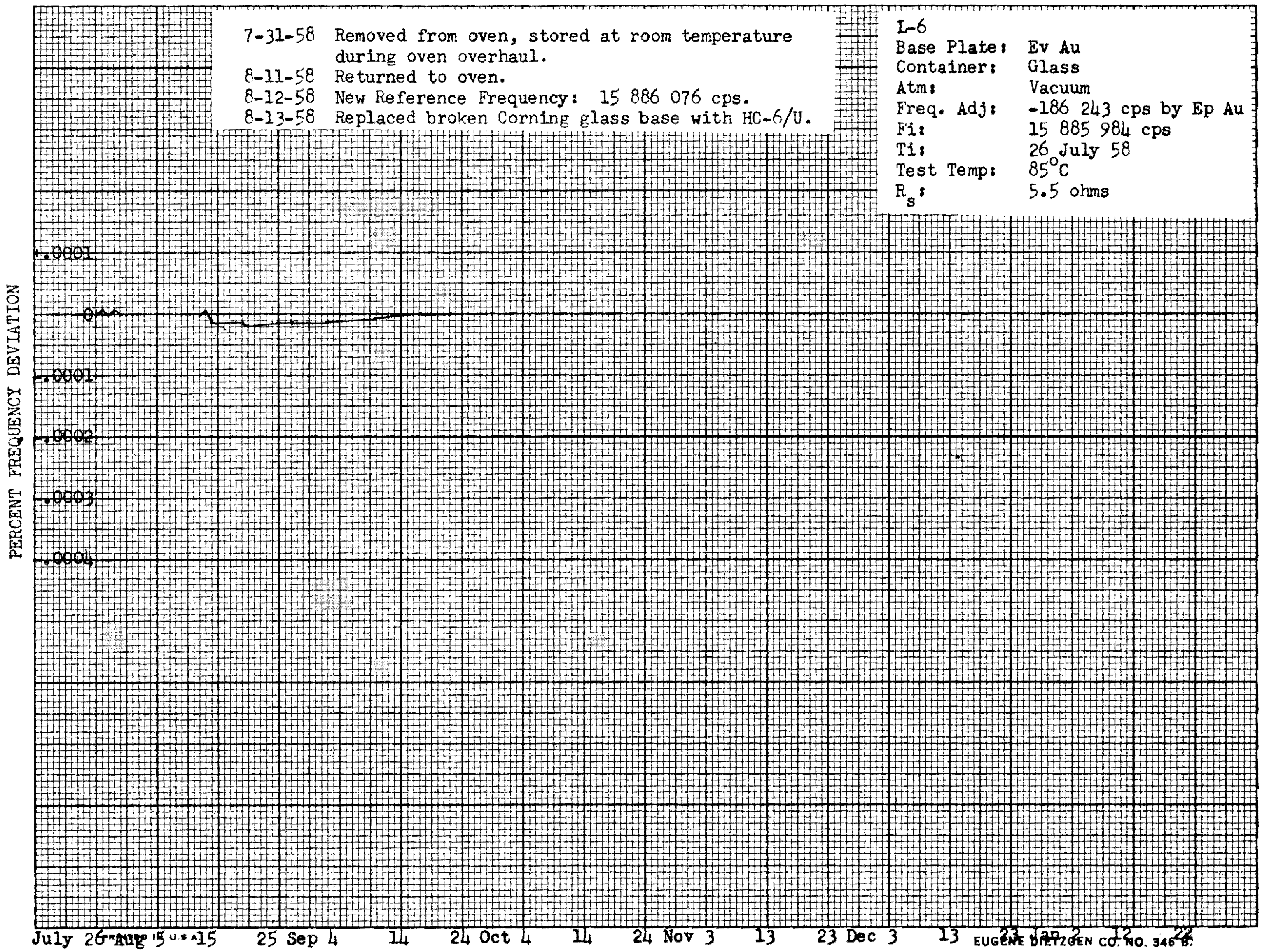


Figure 21. Plot of Frequency Data for Resonator Au-L-6. Overcoated, Glass Container.

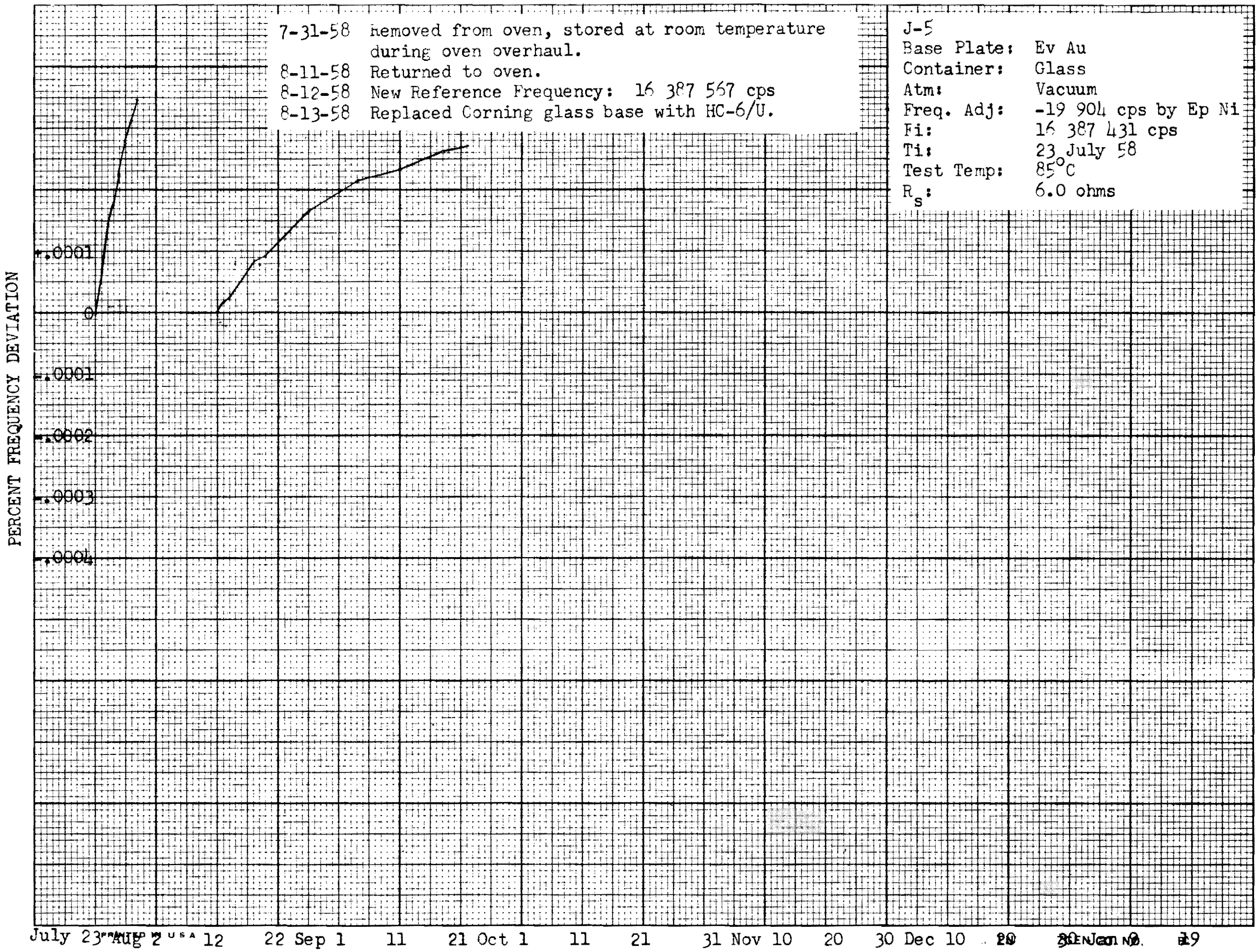


Figure 22. Plot of Frequency Data for Resonator Au-J-5. Overcoated with Electroplated Nickel, Glass Container.

shown in Figure 23 (O-4). Hence, it appears that the upward shift was due to some characteristic of the electroplated nickel films.

Similar upward shifts were exhibited by resonators stressed by spring clips and electroplated nickel films have been reported as being deposited in a highly stressed condition; the stressed condition has been revealed in resistance changes occurring in nickel films subjected to annealing as reported in previous studies made here. Hence, the cited behavior is presently ascribed to stresses in the deposited electroplated nickel films. These stresses, it is conjectured, were subsequently relieved with time. This problem required additional study since it appears pertinent to the present uses of nickel overcoating to frequency. The upward drift may counteract negative drift influences initially but long term stability is unpredictable. It is worthy of note that platinum plated units electroplated with rhodium likewise exhibited distinct upward drifts as reported in the Final Report of Contract No. DA-36-039-SC-64613.

Evidence of alloying or diffusion of atoms of different densities has not yet been established from the frequency behavior of the resonators plated with gold plus nickel. The temperature of the final bake out period, of 3 hours at 185°C, and of the glass sealing operation may have virtually completed diffusion that may have been expected at the operating temperature 85°C.

f. Frequency Changes During Processing

In Quarterly Report No. 3 of this Contract typical frequency changes of resonators occurring during each fabrication step were exhibited in Table III of that report for resonators of groups C_1-1 - C_1-9 and D-1 - D-10. Similar changes for groups made subsequently are exhibited in Table I of the Appendix. These data are included to demonstrate patterns of frequency shift that may be expected of resonators of this frequency range when subjected to the fabrication steps outlined. The only large shift generally exhibited besides that due to overplating was that occurring during canning in the metal can. The reason for this has not yet been determined. A second moderate increase of frequency was exhibited during the final bakeout and seal. This may be attributed largely to desorption of gases or solvent residues from the resonator surface and indicates the importance of this step in the final cleaning of the resonator surface.

E. COMMENTS

Although leaks in many of the 175 resonators examined during the first phase obscured much desirable data concerning the intrinsic frequency stabilities of

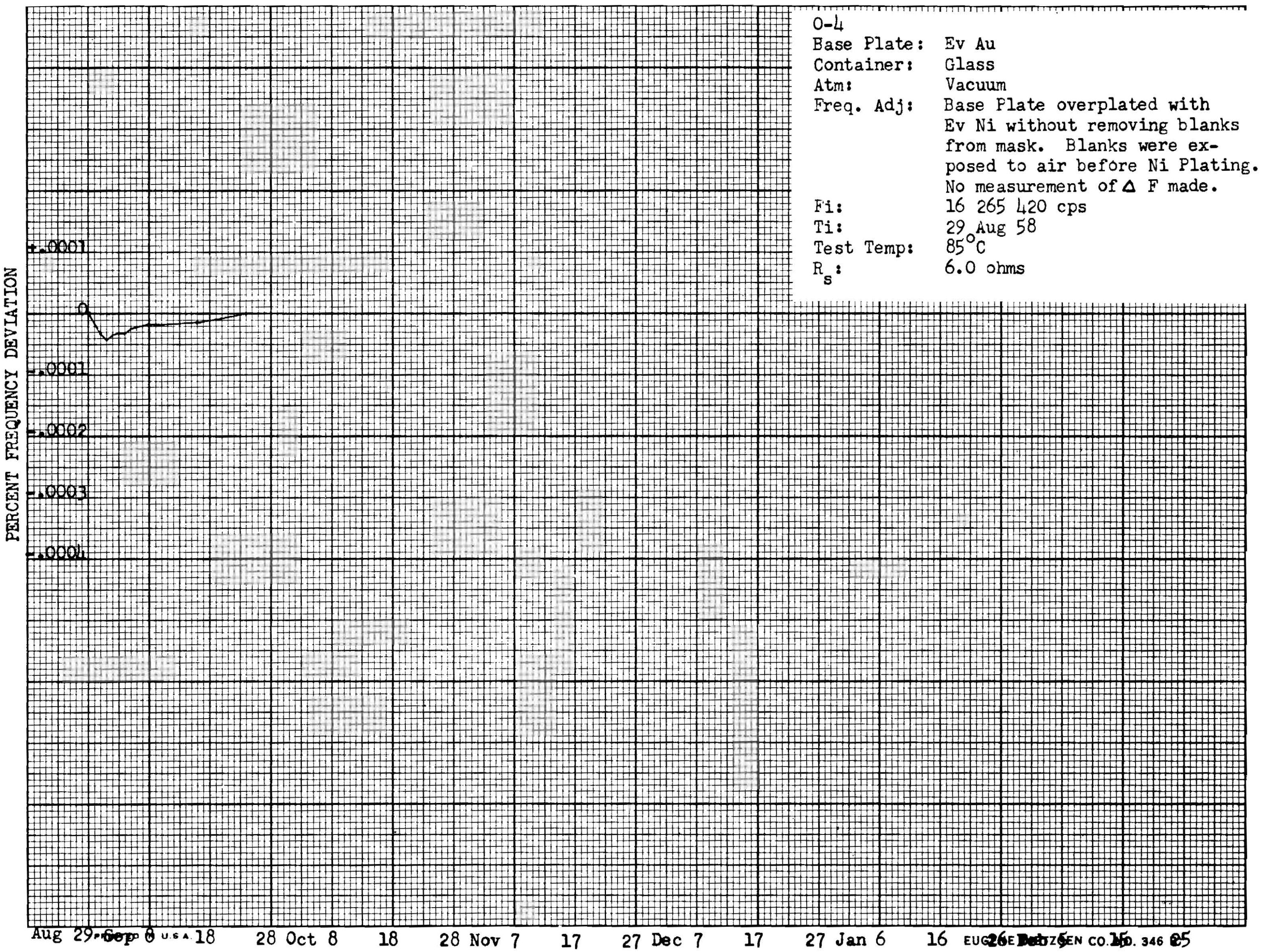


Figure 23. Plot of Frequency Data for Resonator Au-O-4. Overcoated with Evaporated Nickel, Glass Container.

the units under study, sufficient data were obtained to show that overplating a gold plated resonator with evaporated gold for its frequency adjustment should not appreciably degrade the stability of the resonator. Data obtained subsequently from the L group, using electroplated gold as the overcoating material, gave no frequency degradation for electroplated gold overcoats.

Overplating was found superior to positive ion bombardment or Tesla discharge removal of plating as a method of frequency adjustment; in fact, the latter two appeared unsatisfactory unless meticulously controlled for very limited frequency changes of only a few hundred cycles.

Overplating gold plated resonators with electroplated nickel gave units with a distinct upward drift of several parts per million in 30 days. This drift was not experienced when the overcoating was evaporated nickel. The drift is ascribed to residual stress in the electroplated nickel film. Resonators plated by evaporation of aluminum onto the hot quartz blanks did not give stabilities comparable to gold plated units. Drifts of 2 to 6 parts per million were common even for units sealed in glass when operated at $85^{\circ}C$. R_s increases with time of some aluminum plated units appeared to establish a positive frequency drift vector countering the negative one due to corrosion and adsorption. The drift vector due to R_s change may have more significance for units with thin aluminum coatings (1500 angstroms or less) than for units with thick ones (2500 angstroms or more) but should be given consideration in interpretations of stability plots of all aluminum plated resonators.

Limited tests of silver plated resonators plated by the deposition of the silver on the hot quartz substrate disclosed stabilities, in the absence of leaks, comparable to those of gold plated units.

The high incidence of leakers in the HC-6/U containers examined, and the innocuous appearing methods of initiation base cracks and leaks after units have passed inspection tests, require the institution of preventive measures to avoid such occurrences in industry and the field. Sockets, of greater tolerance for the pins, and bases better designed to withstand abuse are recommended.

Glass containers are normally subject only to gross and readily discernible leaks at the time of fabrication and are not subject to subsequent leaks except by obvious fracture. In contrast, leaking of the HC-6/U container is probably one of the greatest causes of instability of units in service, since leaks may develop at any time from a number of inherent weaknesses. The adoption of a glass container is perhaps the only real solution to the problem, and it is therefore recommended for resonators for which long term stability is a critical need.

V. CONCLUSIONS

AT-cut quartz resonators, of 16.5 mc fundamental frequency, base plated with evaporated gold and adjusted to frequency by means of subsequent evaporation or electroplating of gold are intrinsically stable resonators. If meticulously processed, mounted and sealed in the manner described in this report and in the Final Report of Contract No. DA-039-SC-64613 these units should exhibit drifts no greater than one part per million per year. If they are mounted in glass, and hence permanently sealed, this stability should be maintained indefinitely.

Frequency adjustment over large ranges by ion bombardment or Tesla discharge techniques are unsatisfactory from the standpoint of the subsequent stability of the units.

Resonators base plated with silver and processed and sealed with the same degree of care as the gold plated resonators should approach the stability obtained with the gold plated ones.

Resonators base plated with aluminum are intrinsically less stable than those coated with gold or silver but drifts no larger than two or three parts per million per year are now obtainable. Progress to date in stabilizing aluminum coated resonators gives promise that a processing technique may be developed with further work which will result in units approaching the stability now obtainable for gold plated resonators.

Adjusting gold plated resonators to frequency with electroplated nickel subjects them to stresses which may affect the frequency behavior of the resonators. No bimetal pairs should be used on resonators expected to maintain high stability unless the drift effects of the pair have been established and have been found acceptable in carefully controlled experiments.

The high incidence of leaks experienced in resonators mounted in metal containers of the HC-6/U type have again emphasized the probability that leaking is the primary cause of large aging changes for quartz resonators as currently fabricated. For conditions requiring resonators of high and permanent reliability glass containers are recommended. Metal containers and bases of a design specifically shown to minimize leaks formed during or subsequent to sealing are recommended where metal containers are considered necessary.

VI. PERSONNEL

The personnel working on this project and the hours devoted to the work during its course were as follows:

		Hours
Richard B. Belser	Associate Professor, Research Project Director	500
Walter H. Hicklin	Assistant Research Engineer	800
Philip J. Kittel	Research Assistant	1150
Mercer D. Carithers	Technician	500
James W. Johnson	Research Assistant	160
James A. Darnell	Research Assistant	160

VIII. FUTURE PROGRAM

Further work, to establish the maximum stability obtainable with aluminum plated resonators subjected to frequency adjustment and to develop the necessary techniques of fabrication, is recommended.

Establishment of aging standards for commercially fabricated units is desirable, and work on the selection of the HC-6/U container of best current design for leakproof sealing, or on the design of a suitable container to replace it, is recommended.

Metal films or metal film pairs to be allowed as plating for quartz resonators should be specified and the behavior of those selected which has not yet been studied should be established.

Respectfully submitted,

Richard B. Belser
Project Director

Approved by:

J. E. Boyd, Director
Engineering Experiment Station

APPENDIX

TYPICAL FREQUENCY CHANGES DURING CRYSTAL RESONATOR FABRICATION*

Unit	Initial Frequency (~)	Frequency Correction (~)	ΔF Due To Overnight Storage (~) At 60°C	ΔF Due to Sealing Stem To Bulb (~)	ΔF Due** To Final Sealing(~)	Net ΔF Col. 3 To 6 (~)	Base Plate
J-1	16305709	-18893+	-226	-157	+429	+ 6	Gold
J-2	16276513	- 1927+	+ 21	+512	+431	+964	Gold
J-3	16449467	-10501+	-250	+157	+100	+ 7	Gold
J-4	16406208	- 623+	-215	+ 70	+180	- 35	Gold
J-5	16408644	-19904+	-210	-124	+319	- 15	Gold
J-6	16407522	- 2052+	- 34	-2710	+2085	-659	Gold
J-7	16383933	-13864+	-205	-425	+446	-184	Gold
J-8	16460274	-19927+	- 37	-542	----	----	Gold
J-9	16456869	-16624+	-245	-135	----	----	Gold
J-10	16280045	-19200+	-118	-1188	----	----	Gold
J-11	16487301	- 4058+	-171	-181	----	----	Gold
K-1	15930313	- 8525+	----	+ 5	----	----	Gold
K-2	16010313	- 9737+	----	+528	-785	-257	Gold
K-3	16131447	- 9497+	----	-674	+581	- 93	Gold
K-4	16147908	- 8394+	----	+118	+133	+251	Gold
K-5	16000185	-12526+	----	-237	+532	+295	Gold
K-6	15995000	- 4531+	----	-257	+478	+221	Gold
L-1	16114465	- 98710+	----	-127	+350	+223	Gold
L-3	16129791	-473110+	----	+216	+495	+711	Gold
L-4	16064358	-100120+	----	+ 87	+254	+341	Gold
L-5	16061118	-260880+	----	+ 25	+212	+237	Gold
L-6	16073248	-1862450+	----	+160	+153	+313	Gold

* All units mounted in glass. Frequency measurements were made at room temperature. The frequency changes represent that produced by the indicated operation as compared with the last recorded frequency measurement.

** All units sealed in vacuo after baking 3 hours at 180°C and 10^{-6} mm Hg.

TYPICAL FREQUENCY CHANGES DURING CRYSTAL RESONATOR FABRICATION (Continued)

Unit	Initial Frequency (~)	Frequency Correction (~)	ΔF Due To Overnight Storage (~) At 60°C	ΔF Due to Sealing Stem To Bulb (~)	ΔF Due** To Final Sealing (~)	Net ΔF Col. 3 To 6 (~)	Base Plate
M-1	16684666	None	----	----	----	- 39	Aluminum
M-2	16664891	None	----	----	----	- 47	Aluminum
M-3	16685924	None	----	----	----	- 04	Aluminum
M-4	16667824	None	----	----	----	-220	Aluminum
M-5	16682320	None	----	----	----	- 66	Aluminum
M-6	16690430	None	----	----	----	- 89	Aluminum
M_1-1	16674792	None	----	-146	- 57	-203	Aluminum
M_1-2	16648290	None	----	- 30	- 86	-116	Aluminum
M_1-3	16658222	None	----	- 51	- 49	-100	Aluminum
M_1-4	16689081	None	----	- 14	- 71	- 85	Aluminum
M_1-5	16671333	None	----	- 60	- 39	- 99	Aluminum
M_1-6	16657381	None	----	- 61	- 54	-115	Aluminum
M_1-7	16697084	None	----	-222	-120	-342	Aluminum

\+ Frequency corrected by deposition of electroplated nickel.

⊕ Frequency corrected by deposition of electroplated gold.

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2. R. B. Belser, "Study of the Effects of Processing Techniques and Materials on Aging of Quartz Crystal Units," Final Report, Contract No. DA-36-039-SC-64613, U. S. Army Signal Corps, July 1957.

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